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PROCEEDINGS OF THE SOCIETY OF ARTS.

THIRTY-THIRD YEAR, 1894-95.

THURSDAY, April 11, 1895.

THE 472d meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., Mr. N. M. Lowe in the chair.

The records of the 470th and 471st meetings were read and approved. Messrs. Henry S. Adams, of Arlington, C. H. Blackall, of Boston, Albert E. Leach, of Newtonville, Frederick C. Moody, of Boston, and A. C. Thomson, of Brookline, were duly elected Associate Members of the Society.

The following paper was read by title:

"A Discussion of State Legislation on Highways in the United States," by General Roy Stone.

Professor G. F. H. Markoe, of Boston, read a paper on "Essential Oils and their Applications in the Arts, especially in the Manufacture of Perfumes." A large collection of recent synthetic products was shown. The meeting then adjourned.

THURSDAY, April 25, 1895.

The 473d meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., President Walker in the chair.

The records of the previous meeting were read and approved.

Voted, that a committee of five be appointed by the chair to nominate candidates for the Executive Committee for the next year. The President appointed as such committee, Messrs. Desmond FitzGerald, A. Lawrence Rotch, Franklin W. Hobbs, Robert Batcheller, and Dr. R. P. Bigelow.

Mr. Simeon C. Keith, Jr., of the Institute, then read a paper on "Microörganisms of Fermentation and the Danish System of Pure Yeast Culture," illustrated with the lantern. Adjourned.

THURSDAY, May 9, 1895.

The 474th and 33d annual meeting of the SOCIETY OF ARTS was held at the Institute this day at 8 P.M., President Walker in the chair.

The records of the previous meeting were read and approved.

The Chairman of the Nominating Committee reported the following nominations for Executive Committee for the ensuing year: George W. Blodgett, Chairman, C. J. H. Woodbury, Henry M. Howe, Henry H. Carter, and Walter S. Allen.

The Chairman of the Executive Committee reported that the committee nominated Clement W. Andrews for Secretary for the ensuing year.

The reports were accepted, the Society proceeded to ballot, and these gentlemen were declared duly elected.

The report of the Executive Committee was read, in part, as follows:

The Executive Committee of the SOCIETY OF ARTS present the following as their report for the 33d year:

One year since there were 75 life members and 148 associate members, 223 in all. Of the life members, 5 have died; one person has become a life member by the operation of the By-Laws, and the present number is 71.

Of 148 associate members in May, 1894, one has become a life member by the operation of the By-Laws, 12 have resigned, and 2 have died; 48 new members have been elected, and the associate mem-

bership at present numbers 181 — a gain of 33. The total membership is now 252. Compared with last year there is a gain of 29, or 13 per cent.

The attendance has ranged from 30 to 240 persons in 13 meetings, and the average has been 75.

The Executive Committee feel that the Society ought to have a much larger membership, and they, therefore, request each member of the Society to send to the Secretary the names of such suitable persons among his acquaintance as he may find disposed to become members, that they may be acted upon by the Executive Committee.

They would also invite a more full discussion of the papers read and topics presented before the Society.

For the Executive Committee,

(Signed) GEORGE W. BLODGETT, *Chairman.*

The report was accepted and ordered to be placed on file. The report of the Meteorological Committee was read as follows:

BOSTON, May 9, 1895.

The three members of the Meteorological Committee have together inspected the station of the Weather Bureau in this city. As a part of their report to the SOCIETY OF ARTS they present an abstract from the report of the committee to the chief of the Weather Bureau:

"We have the pleasure of reporting that it presented to us the appearance of being kept and conducted in a very orderly and satisfactory manner. We believe the work performed is commendable both for its quality and its quantity, and we also believe it is giving good satisfaction to those in this vicinity who are competent to judge of its merits who may be benefited by its results."

"One of the features of the work which we wish specially to commend is the liberal distribution of the Daily Weather Maps. We understand that the people are learning to appreciate these more and more highly, and that the demand for them is constantly increasing. We are pleased to know that the official in charge of the station has plans in progress for improvements, which, if successful, will increase the rapidity with which the maps may be printed, and will decrease the cost by diminishing their size without thereby impairing their legibility. If his experiments demonstrate the superior efficiency of either of the processes proposed, we hope the Bureau will grant Mr. Smith the opportunity of putting it in practice at this station at which the first local weather maps were produced."

In their report the members of the committee have called special

attention to the emphatic need of better light in one of the rooms of the station, and strongly urged that if a plan for its improvement, which has been submitted, is deemed satisfactory, its adoption be not longer delayed than is necessary.

Respectfully submitted,

(Signed) WILLIAM H. NILES,
GEORGE L. ROBERTS,
A. LAWRENCE ROTCH,
} *Meteorological Committee.*

The report was accepted and ordered to be placed on file, and the same committee was continued.

William J. Jenks, Esq., of New York, Mrs. Ellen H. Richards, of Boston, and Mr. G. V. Wendell, of Boston, were duly elected Associate Members of the Society.

No other business coming before the Society, the President introduced Mr. Henry E. Warren, of Newton, who described and showed in operation the "Thermophone," a new instrument for determining the temperature of a distant or inaccessible place. A paper on the subject, by Messrs. Warren and Whipple, is published in the present number of the *Quarterly*.

The President then introduced Mr. S. P. Fergusson, of the Blue Hill Observatory, who exhibited and explained the meteorograph recently constructed by him for the Harvard Observatory station on El Misti, Peru. Mr. A. Lawrence Rotch described briefly this meteorological station and a similar one on the summit of Mont Blanc, with lantern views.

After a general discussion the President extended the thanks of the Society to the speakers, and declared the meeting adjourned.

CLEMENT W. ANDREWS, *Secretary.*

THE THERMOPHONE, A NEW INSTRUMENT FOR DETERMINING TEMPERATURES.

By HENRY E. WARREN, S.B., and GEORGE C. WHIPPLE, S.B.

Read May 9, 1895.

The thermophone is an instrument for measuring temperature, particularly the temperature of a distant or inaccessible place. It was devised by the writers in 1894 for the purpose of obtaining the temperature of the water at the bottom of a pond. The first experiments were so successful that we were encouraged to study further into the capabilities of the instrument with a view to adapting it to various scientific and commercial uses. Some of the results of our studies and experiments are presented in this paper.

Electrical thermometers may be divided into two classes — thermal-contact, and resistance.

The well-known Le Chatelier pyrometer illustrates the thermal-contact method in the simplest manner. Two wires or strips of dissimilar metals are joined together at one extremity. Their other ends are then connected with a galvanometer by means of copper leading wires. As thus arranged a current is found to flow through the system whenever there is a difference of temperature between the junction of the dissimilar metals and the mean temperature of the other ends of the same. The strength of this current varies almost directly with the difference of temperature, and may be used, with the aid of a galvanometer, to measure the said temperature difference. In practice the ends connected to the leading wires are kept at a nearly constant temperature by putting them in an empty bottle or other inclosed air space. As the instrument is almost always used for very high temperatures it is often assumed that the temperature of these junctions is that of an ordinary living room, say 70° F. Of course an error of a few degrees in this assumption makes little difference when the other ends of the wires are at a temperature of several hundred degrees. On account of the necessary preliminary calibration it is

difficult, if not impossible, to measure temperatures as high as 1,000° C. within 10°. The ultimate standard is the air thermometer, an extremely fussy instrument to use. In this thermal-contact method the very small space taken up by the junction of the two wires and the simplicity of the apparatus make it valuable for obtaining high temperatures; indeed, the junction itself may be plunged into molten metal without affecting the accuracy of the instrument in the least. The greatest objections, perhaps, are the necessity for a sensitive galvanometer, and the space taken up by the same, and the occasional breaking of the wires, which necessitates recalibration. The instrument is not well adapted for obtaining temperatures at any great distance. Ordinarily, when platinum and platinum-iridium wires are used, the curve representing the relation between temperature and galvanometer deflections is nearly a straight line for temperatures higher than 400° C.

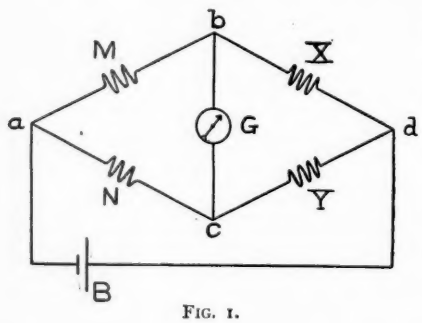


FIG. 1.

The thermopile is an ancient and little used instrument for determining slight changes in temperature. It is the same in principle as the foregoing, but instead of using the junction of two dissimilar strips a great many such strips are connected up in series, just as the zinc and carbon plates of a battery are connected. There are thus two sets of junctions, with a large number of wires running between. Each pair of junctions adds its electromotive force to the others, and the result is an extremely sensitive instrument. Of course the readings depend upon the difference of temperature between the two sets of junctions, and are of no value for getting absolute results. The method has been used almost exclusively for qualitative work.

Before proceeding to a description of some of the resistance thermometers that have been made it will be well to consider an instrument universally used by electricians for the measurement of resistances, namely, the Wheatstone's bridge. This consists of an arrangement of resistances and conductors as shown in Figure 1.

The circuit of a battery, B, is divided between *a* and *d* in such a

manner that a portion of the current is obliged to pass through *acd* and the inserted resistances N and Y, while the remainder of the current passes through *abd* and the resistances M and X. The points *b* and *c* are connected by a circuit, in which is placed a galvanometer, G. By means of Ohm's law it can be shown that when the ratio of the resistances M to N is the same as that of X to Y the potential at *b* will be the same as that at *c*, and no current will pass through the circuit connecting those two points; consequently the galvanometer, G, will show no deflection. In that condition the bridge is said to be balanced, and any one of the resistances M, N, X, or Y may be calculated if the other three are known.

Many resistance methods for the determination of temperature have been used. All depend upon the fact that the resistance of any substance to the electric current varies with the temperature of the conductor. Therefore it is readily seen that any apparatus capable of measuring the resistance of a material may also be used to measure its temperature, because one is a function of the other.

The simplest apparatus for measuring temperatures is an ordinary Wheatstone's bridge, such as has been already described. A coil of insulated copper, iron, or platinum wire is connected to the rest of the bridge by heavy leading wires. The resistance of this coil is measured at a given temperature, say 0° C. Then its resistance at other temperatures may be determined by experiment or by calculation. A curve showing the relation between the temperature and resistance is usually drawn. For certain kinds of work, where time is no object, this arrangement answers well. It is necessary, however, to use a thermometer in connection with the bridge coils in order to obtain absolute results, for the resistance of these coils also varies with the temperature. For measuring temperatures at a distance there is a serious difficulty in the use of this method on account of errors introduced by the changes in temperature of the leading wires. These wires are invariably made of copper, on account of its low specific resistance. As this substance changes its temperature at the rate of about 1 per cent. for every 5° F., it is easily seen that considerable changes in its resistance are liable to take place.

A very great improvement over this primitive arrangement was suggested by Siemens in 1883. His idea was to eliminate the errors introduced by the leading wires by making one of them compensate for the other. This he did in the simplest possible manner by

running the wire which connects one pole of the battery, ordinarily with a point on the line wire near one of the bridge coils, to the distant end of the same line wire, thus throwing it into the other side of the bridge. As a result, any change in temperature caused one lead wire to pull the reading of the instrument in one direction and the other wire to pull it in the opposite direction.

Figure 2 represents Siemens' arrangement as used on the Challenger expedition of 1884. The temperature coil, A, and a coil, B, equal in resistance to A and constructed of the same material, were put into adjacent arms of a Wheatstone's bridge. The other two arms, C and D, were made equal to each other. A sensitive galvanometer, G, was used to indicate when a balance of the bridge had been obtained. The plan of procedure was to immerse the coil B in a tank of water while the coil A was lowered into the sea. In order to find the temperature of the coil A it was only necessary to make the temperature of the water in the tank in which the coil B was immersed such that there was no deflection of the galvanometer. Evidently this temperature was exactly equal to that of the coil A; for, by assumption, the coils A and B were equal in resistance only when at the same temperature. The two leading wires were always of equal resistance, being twisted together and having, therefore, the same average temperature. Good results may undoubtedly be obtained by this method if the operator has sufficient patience. It is slow work, however, for the tank of water must be adjusted in temperature gradually and with great care. A mercurial thermometer must be used to determine the temperature of the water in the tank. The apparatus is not at all portable. It was estimated on the Challenger expedition that five minutes were consumed in setting and five minutes more in reading.

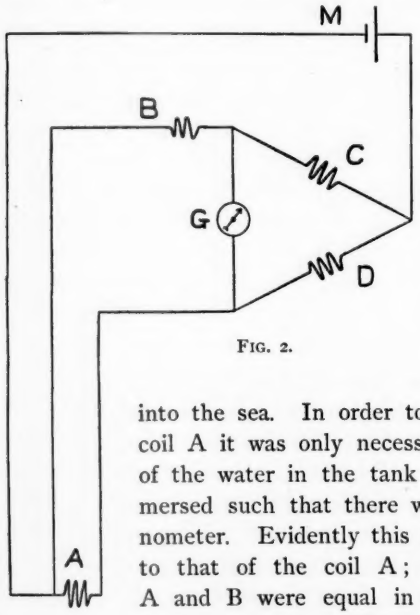


FIG. 2.

An improvement over Siemens' apparatus was made by Hugh Cal-

lendar in 1887. A simplified diagram of his arrangement is shown in Figure 3.

Two coils, A and B, of the same metal — copper, for instance — were arranged on diagonally opposite sides of a Wheatstone's bridge. These coils were exactly equal in resistance when at the same tem-

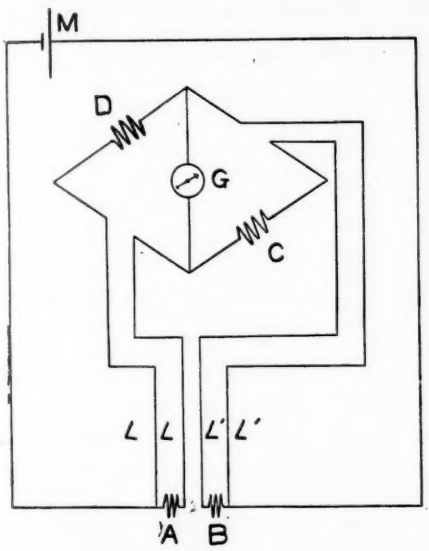


FIG. 3.

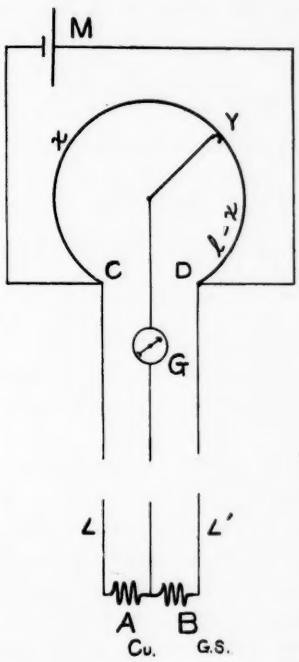


FIG. 4.

perature. The resistances C and D, by a double slide wire, were always exactly equal the one to the other, though variable. With this arrangement it can be shown that the bridge will balance only when A, B, C, and D are all equal. A + B is a function of the temperature; but A + B = C + D and C + D may be read from a scale under the slide wire. Therefore the scale reading is a function of the temperature of A and B. The leading wires, L, L′, produce no effect on the result. By this means absolute and not relative measurements may be obtained, but the apparatus is complex and expensive.

The apparatus invented by the authors of this paper resembles Siemens' more than any other. We have taken advantage of the fact that different metals have different electrical temperature coefficients. The general arrangement is illustrated by Figure 4.

A and B are coils of different metals placed in proximity and joined together as shown in the figure. These coils are connected to a circular slide wire, CD, by means of the leading wires, L and L′. The two ends of CD are put in circuit with a battery, M. A galvanoscope, G, is put into a leading wire connecting the junction of A and B with a movable contact, Y, on the slide wire. The galvanoscope will indicate that no current is passing through this third leading wire when $\frac{A}{B} = \frac{CY}{DY}$. But A and B, having different temperature coefficients, will vary in resistance at different rates with changes in temperature; consequently there will be a different value of $\frac{A}{B}$ for every temperature. The value of $\frac{A}{B} = \frac{CY}{DY}$ may be directly read from a scale placed under the sliding contact, Y, or the temperature corresponding to the given ratio of $\frac{A}{B}$ may be marked upon the scale. In practice the slide wire is wound around the edge of a disk, above which there is a dial graduated in degrees of temperature. The hand on the dial is directly over the movable contact, and both are moved by turning a knob in the center of the dial. For a galvanoscope we have usually found it most convenient to use an ordinary telephone receiver in connection with a circuit breaker.

The operation of taking a temperature reading with the thermophone is as follows: The coils being placed in the spot where it is desired to know the temperature, and the three leading wires being connected to the proper binding posts of the indicator box, the battery current is turned on and the telephone held to the ear. As the hand is moved back and forth over the dial a buzzing sound in the telephone is found to increase or diminish according as the hand approaches or recedes from a certain section of the dial. By varying the position of the hand in this section a point may be found at which no sound is heard in the telephone; at that point the hand of the dial indicates the temperature of the distant coil.

Brief mention should be made of the theory of the instrument. Referring again to Figure 4, CD represents the slide wire, whose length may be called l, and on which Y is the null point. A and B are the resistance coils, made, for instance, of copper and German silver. Let $CY = x$; then $DY = l - x$. According to the theory

of the bridge the resistance of the copper coil, A, is to the resistance of the German silver coil, B, as x is to $l - x$, *i.e.*,

$$\frac{R_{Cu}}{R_{GS}} = \frac{x}{l - x}.$$

If the resistance at 0° C. is called unity, the above formula may be applied to any temperature, t, by inserting the temperature coefficients for the two metals, *i.e.*,

$$\left(\frac{R_{Cu}}{R_{GS}}\right)_t = \frac{1 + 0.003824\,t + 0.00000126\,t^2 + \ldots}{1 + 0.0004433\,t + 0.000000152\,t^2 + \ldots} = \frac{x}{l - x}.$$

Simplified this becomes

$$\frac{x}{l - x} = 1 + 0.0033807\,t - 0.000000391\,t^2 + \ldots.$$

This equation contains but two unknown quantities, t and x; hence by assuming certain values for t we may calculate the corresponding

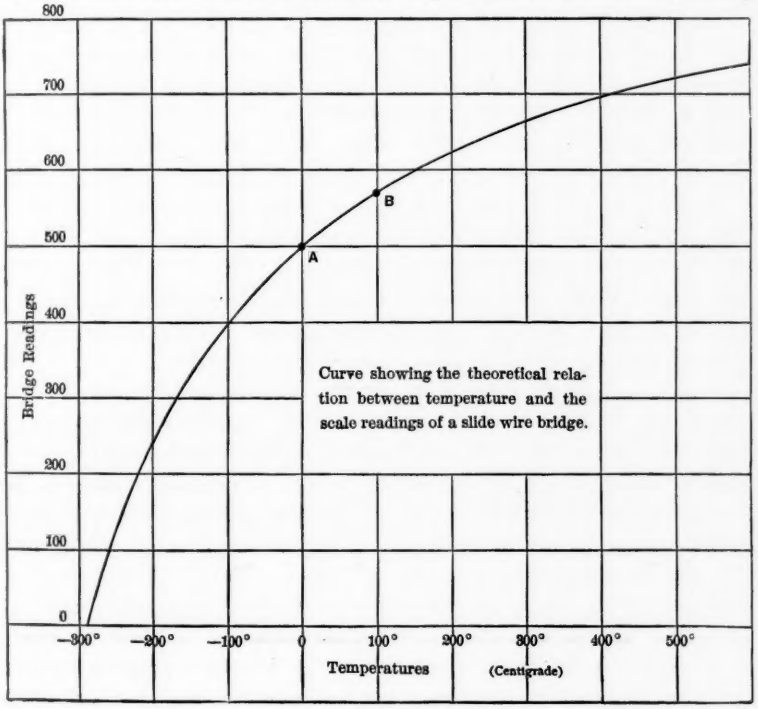


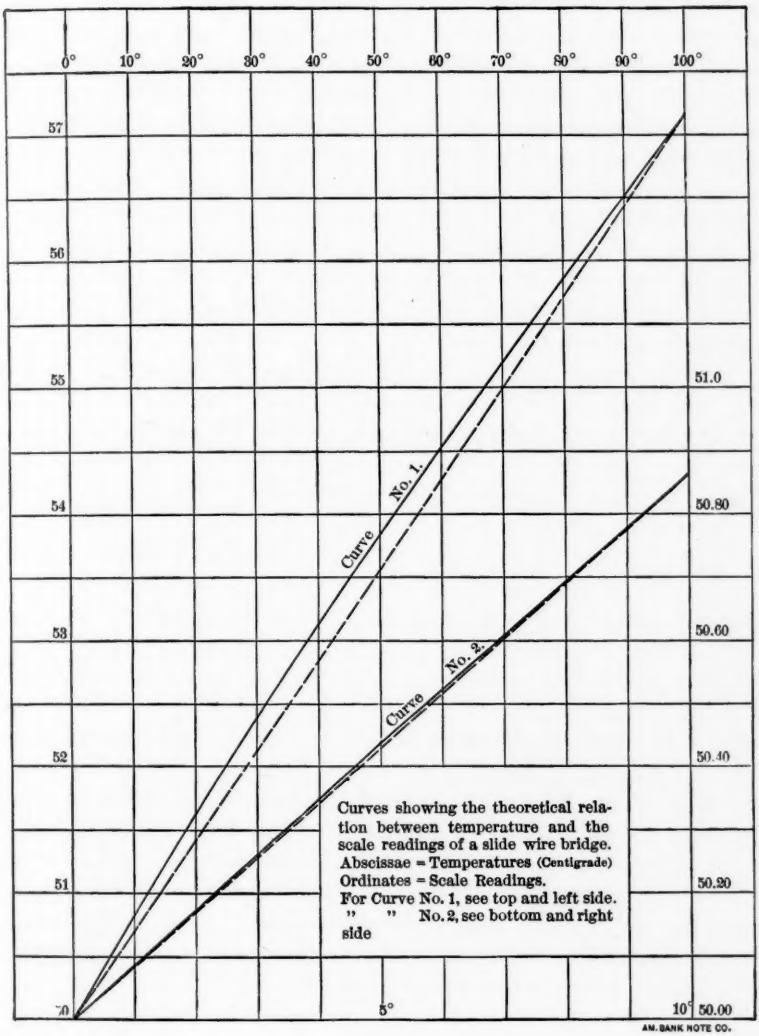
FIG. 5.

values for x; that is, we may find the theoretical bridge reading corresponding to any temperature of the coils, or given any bridge reading we may find the corresponding temperature.

For example, let us assume that the null point, Y, is found at the extreme end of the bridge, at C. In this case $x = 0$, and the corresponding value of t is found to be — 286° C., which is not far from the absolute zero. If we assume that the null point falls at the other end of the slide wire, D, the corresponding value of t is infinity. Between these two points the line representing the relation between t and x will be the curve whose equation is given by the above formula and which is shown in Figure 5. It should be remembered that the above values of the temperature coefficients of copper and German silver apply only between 0° and 100° C., *i.e.*, between A and B on the curve; hence outside of these limits the curve should be considered as approximate.

In Figure 6 will be found the portion of the curve between 0° and 100° C. Not being a straight line, it follows that the length of a degree in one part of the scale will be different from the length of a degree in some other part of the scale. In the same figure is given that part of the curve between 0° and 10° C., and it will be noticed that between these points the curve is almost straight. Therefore for a distance of 10° C. along the scale the degrees might be made of equal length without involving an error greater than about 0.1° C. In practice we have found it an easy matter to determine the 5° points by calibration and then to divide the intermediate space into degrees of equal length. This reduces the error to a point that may be neglected.

The sensitive coils which are located at the place whose temperature is desired may theoretically be made of any two electrical conductors which have different temperature coefficients, though for practical purposes we are limited to the choice of certain metals. It is a singular fact that the electrical temperature coefficients of most pure metals are nearly equal and almost exactly the same as the temperature coefficients of the expansion of gases. The coefficients of the alloys are generally lower than those of their component metals. They also vary to a considerable extent according to their composition. There is much that remains to be known in regard to the electrical temperature coefficients of substances, and the principle of the thermophone may be found useful in pursuing this line of investigation.


0°
10°
20°
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40°
50°
60°
70°
80°
90°
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57
56
55
54
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52
51
50
51.0
50.80
50.60
50.40
50.20
50.00
5°
10°
Curve No. 1.
Curve No. 2.
Curves showing the theoretical relation between temperature and the scale readings of a slide wire bridge.
Abscissae = Temperatures (Centigrade)
Ordinates = Scale Readings.
For Curve No. 1, see top and left side.
" " No. 2, see bottom and right side
AM. BANK NOTE CO.

FIG. 6.

On account of the difference between the coefficients of the alloys and those of pure metals it will usually be found advisable to use some pure metal for one of the sensitive coils and some alloy for the other coil, thus obtaining a couple the ratio of whose resistances changes rapidly with differences of temperature. Other things being equal, the couple which has the greatest differential coefficient will give the most satisfactory results. In the selection of metals to be used, however, there are other qualities which must be taken into consideration, such as specific resistance, permanence, uniformity, cost, etc. Moreover, it is desirable to use metals which are commonly sold in wires of the required size and with the proper insulation, thus avoiding the troublesome delays and extra expense often attending special manufacture.

Of the many possible combinations of metals the following may be considered as particularly important, namely, copper and German silver, iron and German silver, platinum and platinum-iridium, platinum and platinum-silver. Iron possesses several qualities which make it well fitted for use as one of the sensitive coils. On account of its high specific resistance it is particularly suited to cases where it is necessary to put the coils into as small a space as possible, as, for instance, in medical work, or to cases where high resistance coils are required, as in long-distance work. Copper has a slight advantage over iron in being somewhat more uniform in quality, but it has a much lower specific resistance, necessitating a long length of coil to obtain a given resistance. This low resistance may sometimes be an advantage, however, as it gives to the coils a greater radiating surface. The combination which we have selected for use in our low temperature instruments is that of copper and German silver. These metals may readily be obtained in any desired form, their coefficients are favorable, they are not liable to corrode, and they are comparatively cheap. Long experience has proved that they are well adapted to resistance work. For high temperature work it is necessary to use metals which do not easily melt. Either platinum and platinum-silver or platinum and platinum-iridium may be used.

In choosing the amount of the resistance to be used for the sensitive coils two opposing conditions present themselves. The resistance must be kept low enough to get sufficient sensitiveness when using an ordinary telephone, and it must be kept high enough to avoid error caused by the heating of the wires by the battery current. We

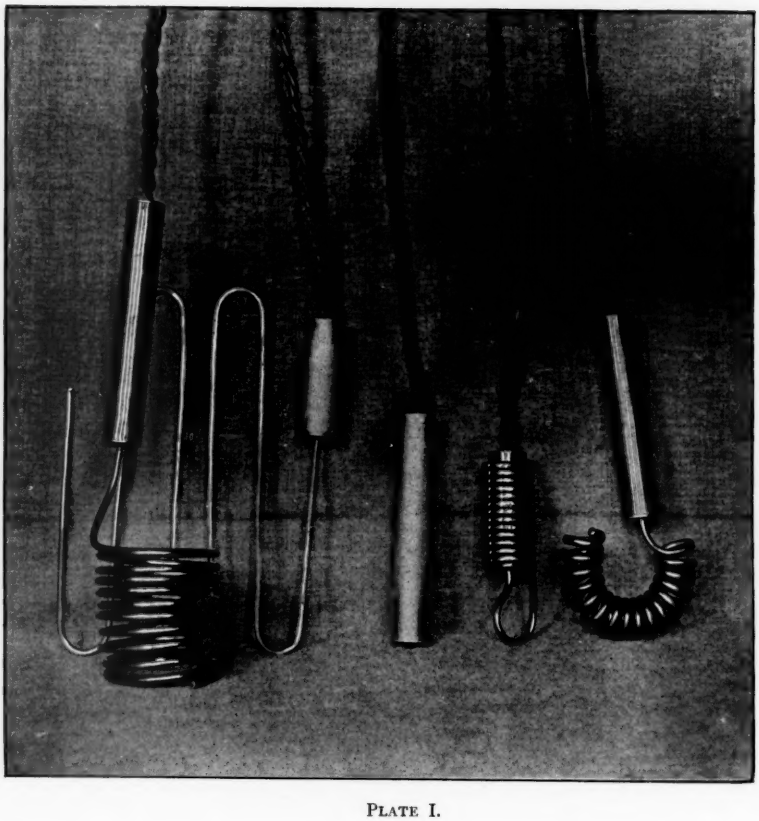

PLATE I.

have selected a value of 100 ohms for each coil as best fulfilling the conditions for ordinary work. There is no difficulty, however, in using coils as low as 25 ohms or as high as 1,000 ohms. Usually it is desirable to make the resistances of the two coils such that they shall be equal at about the middle of the scale which the instrument is designed to read. For ordinary temperatures it is our custom to make them equal at about 50° F.

The method of protecting the sensitive coils is a matter of great importance. They must be kept free from injury and from atmospheric corrosion; they must be so arranged that there may be a ready transference of heat to and from them; they must be suitably connected to the lead wires; and the whole arrangement must be strong and capable of withstanding rough usage.

In our first instrument the sensitive coils were put into a glass test tube, which was afterwards partially filled with oil. Three leading wires insulated with gutta-percha entered at the top of the tube. A mixture of melted paraffine and ground coffee was poured into the top of the tube and allowed to harden, in order to form a water-tight seal. This coil was used in connection with an ordinary slide wire bridge to determine the temperature at the bottom of a lake. The objections to the glass tube were soon apparent, and the broken relic has now only a historical value. A thin brass tube, 1 inch in diameter, was then substituted for the glass one, and alternate layers of vaseline and paraffine used as a seal. The greatest objection of this form was found to be the slowness in setting. The next step was to use a small, thin brass tube $\frac{3}{16}$ inch in diameter and 8 feet long. Into this the resistance wires were drawn, after which the tube was coiled into a helix about 3 inches in diameter. One end of this small tube was made to enter a short piece of brass tube 1 inch in diameter, where connections with the leading wires were made. The small tube was then filled with oil, by means of an aspirator, and sealed. The end of the large tube where the leading wires entered was then effectually sealed by pouring in molten tar and afterwards covering with a layer of plaster of Paris. This arrangement answered the purpose admirably, possessing remarkable quick-setting properties, which will be described later on. Coils of this type have since been used in most of our instruments, a few changes having been made in the method of sealing the tubes where the leading wires enter. The photograph on Plate I shows several coils of different design.

The indicating part of the thermophone consists of a circular form of slide wire bridge. Three thin mahogany discs from 3 to 5 inches in diameter are fastened together as shown in the photograph on Plate II. The lower one carries upon its periphery a German silver slide wire, the ends of which are electrically connected at two convenient binding posts with the two main lead wires. Over this slide wire a spring contact, which is in reality the terminal of the telephone circuit of the bridge, is free to move. This contact is carried on a radial arm attached to a spindle, which passes through all three of the discs, terminating in a vulcanite knob. To this spindle there is also attached a pointer, which moves over a suitably graduated dial on the upper and larger of the three discs. By turning the knob the pointer may be moved over the dial at the same time that the contact moves over the slide wire. The German silver wire which is coiled around the edge of the lower disc is only a small part of the whole slide wire, which is usually of considerable length. Only the middle portion of the slide wire is in active service, the unused portions of the wire being coiled around the inner disc in order that it may be compact, out of the way, and at the same time have a uniform temperature throughout its entire length.

The length of the slide wire is a matter of great importance, for it determines the scale of the instrument. The longer the slide wire the less the proportion of it in active service, and consequently the less the range of the instrument. The actual length of the slide wire necessary for any particular scale may be calculated approximately by the following formula:

$$L = \frac{2000}{T} + 2$$

where L equals the total length of slide wire in multiples of its active portion and T equals the scale of the instrument in numbers of Fahrenheit degrees. For example, if the active portion of the wire is 1 foot and the range of the instrument is 130°, $L = \frac{2000}{130} + 2 = 17.4$. The length of the slide wire is therefore 17.4 feet.

In order to protect the slide wire and its contact from injury the discs are usually inclosed in a brass case, having a glass front over the dial. In the portable instruments this brass case is fastened directly to the box containing the battery, but for permanent instal-

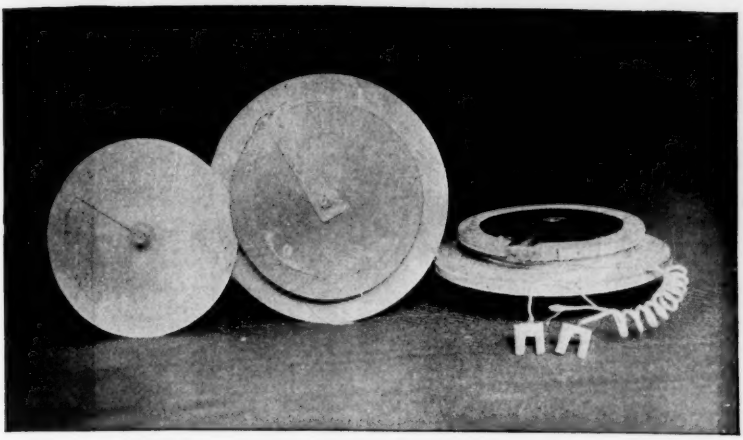

PLATE II.

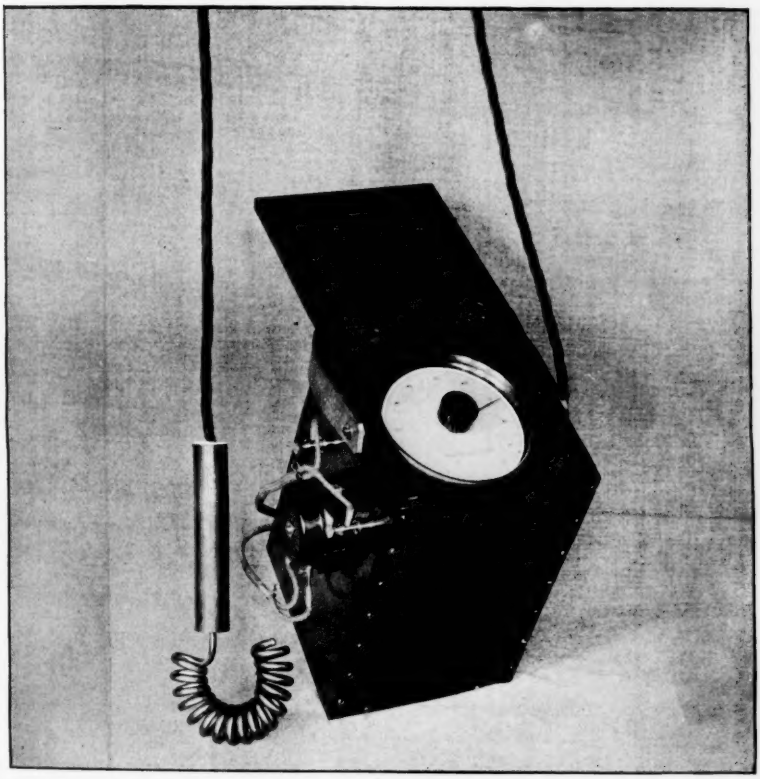

PLATE III.

lations it may be fastened to an ornamental baseboard and screwed to the wall, the battery being located elsewhere. Plate III is a photograph of one of the portable instruments.

One of the most important parts of the thermophone is the current interrupter or buzzer. By its use in connection with the telephone receiver it is possible to avoid the use of a delicate and expensive galvanometer. More than anything else it is the use of this combination of buzzer and telephone which makes the thermophone a portable instrument. By its use exceedingly slight currents of electricity may be detected, and there seems to be no reason why a similar instrument may not be found useful in physical laboratories. The arrangement of the buzzer will be readily understood from Figure 7.

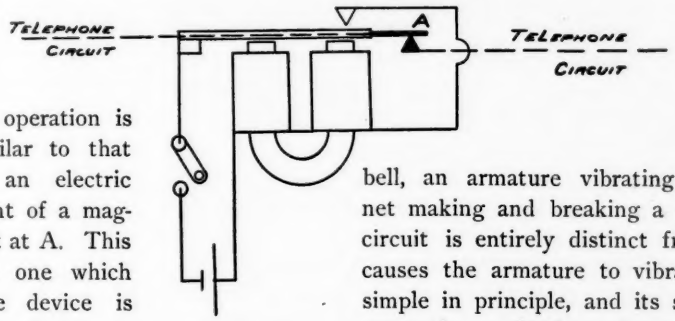

FIG. 7.

Its operation is similar to that of an electric bell, an armature vibrating in front of a magnet making and breaking a circuit at A. This circuit is entirely distinct from the one which causes the armature to vibrate. The device is simple in principle, and its success depends upon the perfection of certain details of construction.

The battery usually consists of three dry cells. In one instrument, which has been used daily for more than six months, the cells show very little loss of power. The battery current may be turned on or off by means of a switch placed directly over the telephone holder on the side of the box.

In any telethermometer of the resistance type it is of the utmost importance to so arrange the leading wires that changes in their temperature shall not appreciably affect the reading of the instrument. In designing the thermophone this fact was kept in mind, and the resulting arrangement of the electrical parts appears to be quite satisfactory.

It will be remembered that there are three leading wires between the indicator and the sensitive coils. Two of these, which may be called the main leads, run from the ends of the slide wire to the free

ends of the copper and German silver resistances. The third, which connects the junction of the two said resistances with the movable contact on the slide wire, has in its circuit the telephone and interrupter. Recalling the arrangement of the Wheatstone's bridge, it will be seen that one of the main leading wires is in one arm of the bridge, while the other main lead is in the adjacent arm; hence any change in the resistance of one will tend to be neutralized by a similar change in the resistance of the other, assuming that the two leads have the same average temperature. An equality of temperature, and consequently of resistance, is brought about by keeping the two wires side by side. Usually it is convenient to have the three leading wires twisted or braided together. It goes without saying that each leading wire should be thoroughly insulated.

How far the two main leading wires tend to neutralize each other and to give a reading free from error may be shown by the following demonstration: To determine the safe allowable resistance of the leading wires let

R_1 = the resistance of each leading wire.

Δ = the allowable error in temperature measurement in Fahrenheit degrees.

S = the total range of the instrument in Fahrenheit degrees.

A = the resistance of the copper coil, including R_1.

B = the resistance of the German silver coil, including R_1.

δ = the greatest change that will ordinarily take place in R_1 under ordinary atmospheric conditions. If the leading wires are of copper, and if the range of atmospheric temperature is assumed to be 100°, $\delta = \frac{R_1}{10}$, because the electrical temperature coefficient of copper is such that a change of 5° F. produces a change of about 1 per cent. in resistance; a change of 100°, therefore, causes a change of 20 per cent. resistance, or a change of 10 per cent. above and below the resistance of the coil at 50°.

If we take the case where the leading wires are at one of the assumed points of extreme variation, namely, 0° or 100° F., we shall have the true ratio of the sensitive coils shown by $\frac{A}{B}$, while the apparent ratio given by the indicator will be

$$\frac{A+\delta}{B+\delta} = \frac{A\left(1+\frac{\delta}{A}\right)}{B\left(1+\frac{\delta}{B}\right)} = \frac{A}{B}\left(1+\frac{\delta}{A}-\frac{\delta}{B}+\cdots\right).$$

The difference between the true and apparent readings is then, approximately,

$$\frac{A}{B} - \frac{A}{B}\left(1 + \frac{\delta}{A} - \frac{\delta}{B}\right).$$

Therefore

$$\Delta = 500\left\{\frac{\frac{A}{B} - \frac{A}{B}\left(1 + \frac{\delta}{A} - \frac{\delta}{B}\right)}{\frac{A}{B}}\right\} = 500\left(\frac{\delta}{B} - \frac{\delta}{A}\right),$$

approximately. If we assume that the German silver coil remains constant in resistance (its coefficient is about one tenth that of copper), $A = B\ (1 + .001\ S)$, approximately. Therefore

$$\Delta = 500\,\delta\left(\frac{1}{B} - \frac{1}{B\ (1 + .001\ S)}\right) = \frac{500\,\delta \times .001\ S}{B\ (1 + .001\ S)},$$

approximately. If we neglect $.001\ S$ in the denominator

$$\Delta = \frac{0.5\,\delta\,S}{B} \text{ and } \delta = \frac{2\,\Delta\,B}{S}.$$

Ordinarily

$$\delta = \frac{R_1}{10}, \text{ hence } \frac{R_1}{10} = \frac{2\,\Delta\,B}{S} \text{ and } R_1 = \frac{20\,\Delta\,B}{S}.$$

In order to take a practical example, let us suppose that it is desired to find the size of lead wire to be used in obtaining deep sea temperatures. Suppose that it is desired to have the readings correct within 0.05° F. over a range of 20° F. and that the extreme variation of the temperature of the leads is 20° F. These limits are ample for this case. If a 200-ohm coil were used, $\Delta = 0.05$, $B = 200$, $S = 20$, $\delta = \frac{R_1}{50}$. Substituting these values in the formula $\delta = \frac{2\,\Delta\,B}{S}$, we find that $R_1 = 50$ ohms. Since No. 18 copper wire has a resistance of about 35 ohms per mile, that size of wire may be used for a depth of one mile with a considerable margin of safety. For greater depths it is not necessary to increase the size of the leading wires, but simply to increase the resistance of the sensitive coils, and this may be done up to 1,000 or 10,000 ohms, if necessary.

The question naturally arises as to how the dial is graduated and the instrument standardized. On account of the fact above mentioned, that the degrees are not of the same length in all parts of the scale, it is impossible to graduate the instrument by determining the read-

ings in boiling water and in melting ice and preparing a scale of equal division between them. It is necessary to make comparisons with an accurate mercurial thermometer as the standard for ordinary temperatures. The operation of graduating the dial consists in putting the sensitive coil and the standard thermometer together in a bath having a certain temperature, say 20°, and in noting the position of the pointer on the dial when the telephone is silent; then changing the temperature of the bath to, say 25°, and finding a new position of the pointer, and so on determining the position of points five degrees apart. Between these points the spaces may be divided into degrees of equal length without introducing a sensible error. The melting point of ice and the boiling point of water may be obtained in the usual way. For extremely high and for very low temperatures mercurial thermometers are inaccurate, and we are thus left without a ready standard of comparison; but by extending the theoretical curve of the differential coefficients in both directions, and by using this in connection with known boiling points, it seems likely that we may obtain results equal if not superior to those given by any known instrument.

The thermophone is extremely sensitive. The differential temperature coefficient of the metals is such that the resistance ratio changes about 1 per cent. for each 5° F., this being far above the rate of expansion of solids or liquids. Moreover, slight differences in resistance may be measured easier and with greater accuracy than small changes in length or volume. With thermophones of the atmospheric range, *i. e.*, from — 15° to 115° F., temperatures may easily be taken to 0.1° even by an inexperienced observer. With an instrument of less range, or with one of the same range but having a larger dial, the degrees are longer, and consequently a greater sensitiveness may be obtained. Our standard thermophone has a dial 8 inches in diameter, and readings may be taken to $\frac{1}{15}$° F.

As far as possible we have endeavored to make the parts of the thermophone interchangeable; that is to say, so that any coil may be used with any indicator. In order to do this the ratio of the copper and German silver coils must be the same for every instrument at every temperature. When the coils are manufactured and before they are sealed this ratio is regulated approximately at the temperature of the room. After being sealed they are put into a bath with a standard coil and their ratio finally adjusted by adding a short length of German silver wire to one or the other of the main lead wires.

This involves no error. The indicators are made alike by comparing them at the 5° points with the standard instrument.

One very important quality of the thermophone is the rapidity with which it sets. By covering the sensitive coils with substances having good heat-conducting powers, by making the mass of this protective covering as small as possible, and by giving it a great radiating surface, we have succeeded in producing an instrument which will set quite as rapidly as a mercurial thermometer. The following table shows a comparison between the time of setting of a thermophone and one of Green's chemical thermometers. The figures represent the average of several sets of observations:

TIME OF SETTING. COMPARISON BETWEEN THERMOPHONE AND THERMOMETER.

Time in seconds.	Thermophone.	Thermometer.
0	70.8°	68.9°
10	46.7°	36.3°
20	36.7°	33.0°
30	33.2°	32.7°
40	32.5°	32.5°
50	32.4°	32.4°
60	32.3°	32.4°
70	32.1°	32.3°
80	32.0°	32.3°
90	32.0°	32.2°
100	32.0°	32.1°
110	32.0°	32.0°

The experiments were made by transferring the instruments from a water bath of about 70° F. to a mixture of melting snow, the temperature of which was known to be exactly 32°. The mercurial thermometer fell rapidly at first, reaching 33° in 20 seconds; after that it dropped slowly, requiring 110 seconds to reach the exact temperature. The thermophone, on the other hand, dropped more slowly at first, requiring 30 seconds to reach 33.2°, but it fell more rapidly over the

remaining tenths, reaching the freezing point in 80 seconds, which was one half a minute less than was required by the thermometer.

For obtaining deep sea temperatures a quick-setting instrument is of advantage, because it effects a great saving of time and, consequently, of expense. The Negretti and Zambra thermometer, which is the one usually used by the government for deep sea work, sets very slowly. Dr. Kidder, in his report on thermometers used by the United States Fish Commission in 1885, mentions two experiments which were made to determine the time of setting of the Negretti and Zambra instruments. These thermometers, it will be remembered, are mercurial ones, having a large cylindrical bulb. Just above the bulb the tube has a peculiar bend, where the mercury column breaks when the thermometer is inverted. Readings are obtained by inverting and allowing the mercury above the bend to fall to the other end of the tube, where suitable graduations are made. Of the two thermometers tested by Dr. Kidder one required seven minutes and the other fifteen minutes to register the correct reading when changed from a bath of about 70° to one of melting ice. When these thermometers are used in practice it is customary to allow them to set ten minutes before inverting. This is in striking contrast with the quick-setting thermophone.

The uses of a thermophone are almost as varied as the uses of a thermometer. Aside from its scientific applications, many of which will naturally suggest themselves, we may call attention to a few of its commercial uses.

In connection with the ventilation of buildings it possesses qualities which make it more valuable than the ordinary telethermometers. Besides being accurate and comparatively inexpensive, it has the advantage that any number of sensitive coils may be connected to one indicator. Thus in a large schoolhouse a sensitive coil may be located in each room and the leading wires carried to a single indicator in the janitor's office, where by using a switchboard the janitor may from the one dial ascertain the temperature of any room in the building. The temperature of dark and inaccessible air flues may also be easily obtained. When several sensitive coils are located near together a considerable saving of expense in the wiring may often be made by connecting the copper resistances of all the sensitive coils to one main leading wire and the German silver resistances to the other main leading wire, these leads being carried to the ends of the slide wire of the

indicator. The telephone lead from each sensitive coil is carried to the switchboard near the indicator, where by changing the switch one after another of the coils may be thrown into use. Thus the total number of wires between the coils and the indicator is equal to the number of coils plus two.

In public buildings it will probably be advisable to dispense with the telephone and circuit breaker and use a galvanometer so arranged that the temperature of the distant coil shall be indicated by the deflections of the needle. In such an arrangement it is only necessary to press a button in order to have the needle automatically indicate the temperature. A thermophone of this kind is now in use at the Massachusetts State House.

It is possible to make the thermophone self-recording, and we expect that such an instrument will soon be perfected. It will doubtless find an immediate use in cold storage warehouses.

Among the uses of a high temperature instrument may be mentioned that of obtaining the temperature of flue gases in chimneys. This temperature is intimately connected with the economical operation of a boiler, and at the present time the methods of obtaining it are either very crude and inaccurate or exceedingly troublesome. With one of the coils located in the flue and the indicator in the engineer's office one could easily tell at any time how much heat was being wasted up the chimney. If a self-recording instrument were used the results would be of great value.

As we have already stated, the thermophone was first used to determine the temperature of the water at various depths in Lake Cochituate, one of the sources of the Boston water supply. It proved to be peculiarly well adapted for doing that work, and there seems to be no reason why it might not be used for obtaining temperatures at very great depths. When compared with old deep sea thermometers, or even with those now used, it will be found to possess many points of superiority, among which may be mentioned the following:

1. It is extremely sensitive and accurate.
2. It is independent of pressure.
3. It is very quick-setting and may be quickly read.
4. It does not have to be drawn to the surface when readings are taken.
5. It is portable.
6. No mercurial thermometers are used in connection with it.
7. There are no instrumental corrections to be applied.

In order to show what may be done with the thermophone in the way of studying the temperature of water at various depths, we present in Figures 8, 9, and 10 some of the observations which have been made. The curves were selected with the idea of showing the capabilities of the instrument rather than throwing light upon the complex problem of the distribution of heat in the water of a pond. Most of them, however, are typical curves for the different seasons.

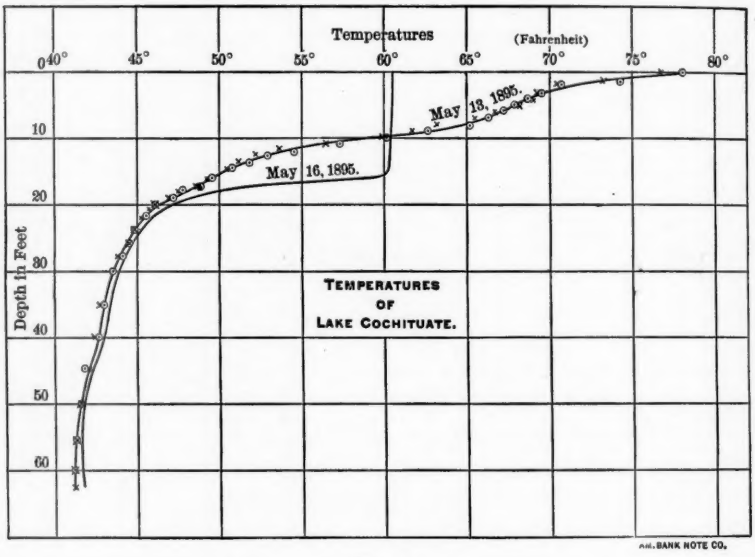

FIG. 8.

It is a well-known fact that in deep ponds there is usually a great difference of temperature between the water at the surface and that at the bottom, this difference being greatest during the summer. In most ponds which are more than 25 or 30 feet deep the temperature at the bottom remains almost constant from April to October, while that at the surface rises and falls with the temperature of the air. The temperature found at the bottom during the summer depends chiefly upon the depth of the pond and upon the temperature of the air and the force of the wind during the month of April, or during that season when the surface water begins to warm up. For instance, it has been found by observations in Lake Cochituate that

as soon as the ice breaks up in the spring the water circulates freely throughout the vertical, the temperature at the top and bottom being almost exactly the same. As the season advances the water grows warmer at all depths. If there were no wind the temperature at the bottom would cease to rise as soon as it had reached the point of maximum density, *i. e.*, 39.2° F., but because of the wind, and because in that part of the temperature scale the difference in density per degree is very slight, the temperature at the bottom rises higher than 39.2°. It continues to rise as long as the difference in density between the water at the surface and that at the bottom does not exceed such an amount that the wind is not able to keep the water in circulation. For Lake Cochituate, which is 60 feet deep, this difference of density is equivalent to a difference of about 5° of temperature. If, however, the winds are unusually high a somewhat greater difference is necessary to prevent circulation. Stagnation of the lower layers having once begun, the temperature at the bottom changes very little during the whole summer. Thus it will be seen that if the warm weather of spring appears suddenly the required difference of temperature between the upper and lower layers is soon obtained, and in consequence there is a low temperature at the bottom during the summer; but if, on the other hand, the season advances gradually the temperature at the bottom will remain at a somewhat higher point. Ordinarily the bottom temperature of Lake Cochituate lies between 42° and 45°, but during the present season, on account of the remarkable hot weather in May, it stands at a somewhat lower figure.

In Figure 8 are given two curves which represent the temperature at different depths in Lake Cochituate, and which may perhaps be considered as typical summer curves. On May 10, 1895, two sets of observations were taken at points about 200 feet apart, one set being indicated by the circles, and the other by the crosses. The two sets of observations agree very closely, showing the great precision which may be obtained with the thermophone. May 10 was a hot, calm day, the maximum air temperature being over 90°; the surface of the water was like a mirror — for several days previous the weather had been warm, with little wind. As a result the temperature curve was a very smooth one. This curve may well be contrasted with the other one taken six days later, namely, on May 16. In the interval between the two sets of observations there were several days of cold, windy weather, with sharp frosts. The result was that the surface cooled

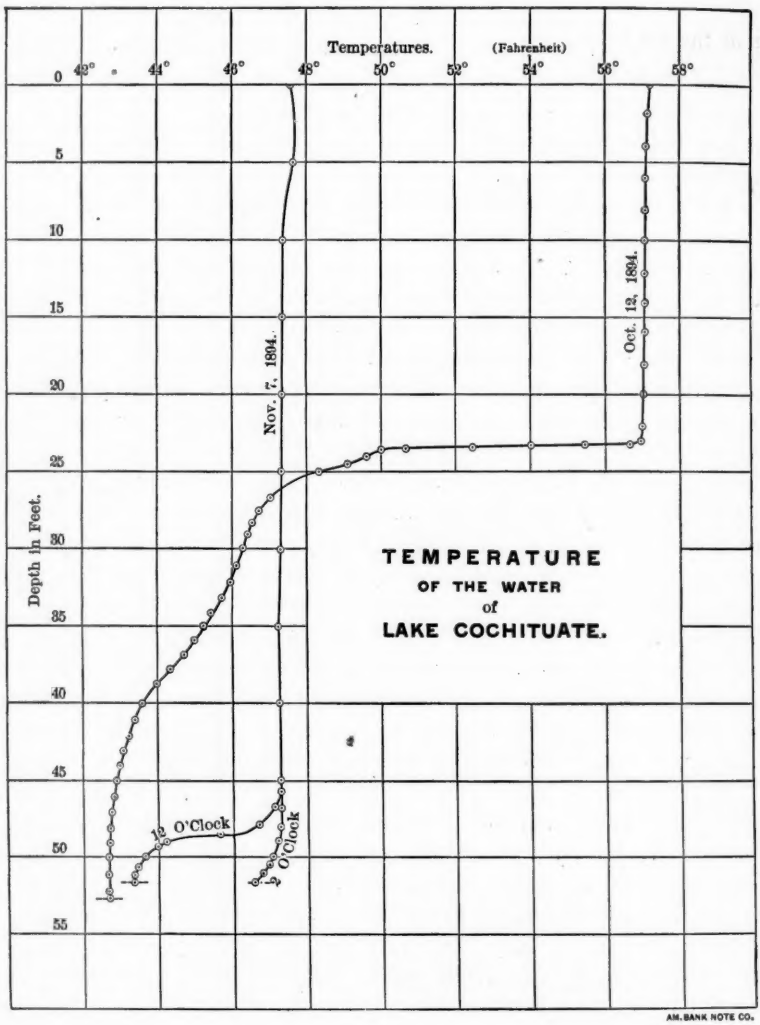

FIG. 9.

off rapidly and the water became stirred up to a considerable depth. The active circulation caused by the wind evidently extended to a depth of about 16 feet, but what may be called an "induced circulation" extended to a somewhat greater depth.

Ordinarily the influence of the wind during the summer is felt only

to a depth of some 10 or 20 feet, but in the fall, when the surface water cools and its density becomes more nearly like that of the lower layers, the wind stirs up the water to greater and greater depths. Finally, when the temperature of the surface has fallen to a point only a few degrees above that of the bottom, circulation takes place throughout the whole vertical. This phenomenon is known as "the turning-over." The temperature changes that take place during this period are illustrated in Figure 9.

The observations on October 12, 1894, showed that down to a depth of 23 feet the water was practically of a uniform temperature; at that depth there was a sharp boundary line between the warmer water above and the cooler water below. The temperature at 23 feet was 56.95°; at 24 feet it was 49.65°, a difference of 7.3° in one foot. Below 25 feet the temperatures decreased gradually to the bottom, observations taken at 1-foot intervals giving a very smooth curve.

On November 6 there was a snow-storm, accompanied by a high wind, which continued for several days. On November 7 observations were again taken at the same place. The temperature was found to be 46.7° down to a depth of 46 feet; from that point to the bottom there was a slight decrease. At noon the temperature at the bottom was 43.5°. Between 46 feet and the bottom the water was plainly in a state of commotion, readings at any one point frequently changing several degrees in less than a minute. At two o'clock the turning-over had been practically completed, and, except at the bottom, where the coil was partially immersed in the mud, the temperature readings were the same from the top to the bottom. It was a most singular coincidence that we should happen to make our observations at the very moment when the turning-over was completed.

The temperature curves obtained during the winter when the surface is frozen are quite different from the foregoing. Three of these curves are given in Figure 10. The middle curve shows the temperature of Lake Cochituate on December 21, 1894, a few weeks after the ice formed. Two sets of observations were taken at points 200 feet apart. One set is indicated by the circles and the other by the crosses, and it should again be noticed how closely the two sets of observations agree. This curve may be said to be the normal type of curve for a frozen lake in this vicinity, the characteristics being a rapid rise of temperature during the first 5 feet below the surface, and below that point a gradual increase towards the bottom, where the temperature tends to stay at its point of maximum density. On

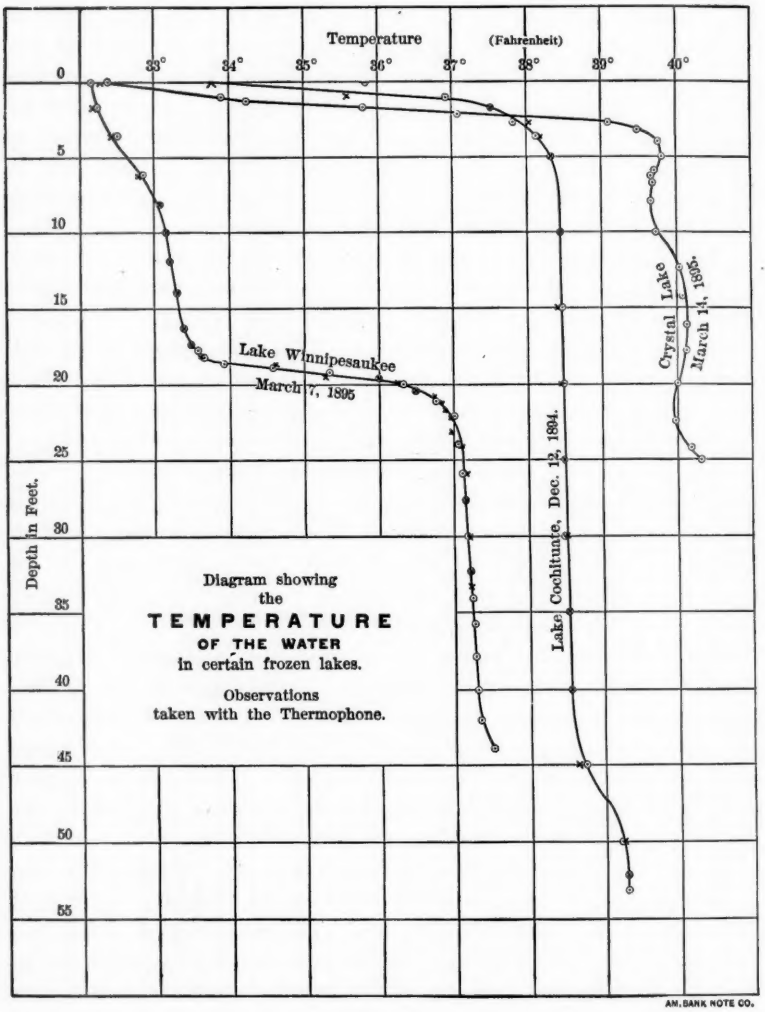

FIG. 10.

account of certain local causes, however, this bottom temperature is sometimes found to be above or below that point.

The right-hand curve represents the temperature of the water of Crystal Lake in Newton Centre, Massachusetts, on March 14, 1895, and illustrates the case of a pond fed by springs. The tempera-

ture was higher than in Lake Cochituate, being about 1° above maximum density, except for a few feet immediately under the ice. The curve is more irregular than the other curves on account of the varying currents from the springs.

The curve on the left represents the temperature of the water of Lake Winnipesaukee at a point east of Long Island and about equidistant from Ragged, Cow, and Little Bear Islands. The observations were taken at a place where a strong current from Moultonborough Bay sweeps into the Broads. The effect of this current is seen in the shape of the curve, which bends sharply at a depth of 18 feet. At a depth of 22 feet it bends sharply in the other direction; below that depth the water has almost a uniform temperature to the bottom. It is evident that there was a layer of cold water flowing over a body of warmer water, the very slight difference between the density of the two layers being sufficient to prevent them from mixing. It will be observed that the bottom temperature is below that of maximum density. This fact has been observed elsewhere. It may be accounted for by the high winds which blow over the lake just before the surface freezes. Even after the water has cooled to the point of maximum density the wind keeps the water in circulation, and causes it to cool still further at all depths until the surface freezes and puts a seal upon further change.

It would be a matter of no little interest to locate some of the thermophone coils in and immediately under the ice of a frozen lake, where there is little current, and note the changes that take place during the freezing and melting of the ice. Such an experiment might easily be made. It has also been suggested that the instrument might be used to obtain the temperature of the ice in glaciers at depths below the surface.

From the curves given above, as well as from many other observations that have been taken, it is seen that the thermophone, by reason of its extreme sensitiveness, may well be used as a current detecter. The following incident illustrates this use: On one occasion observations were being made in Lake Cochituate at a point about 100 feet from the effluent gatehouse. Readings were taken at intervals of 1 foot, beginning at the top. On checking the readings as the coil was being drawn up it was found that for a considerable distance down from the surface the readings did not agree with those previously taken. After some little searching for the cause of the supposed error it was discovered that the boat had shifted its position into

the current that was setting in towards the gatehouse. On rowing back to the original spot readings were obtained which agreed with those taken at first.

The subject of the temperature of the soil at various depths has been studied carefully and thoroughly as far as the use of mercurial thermometers would permit, but obviously such thermometers are not suited to the case. What is needed is a thermometer that can be located in what is practically undisturbed soil and allowed to remain there for a long time without being removed or interfered with in any way. As we believed that the thermophone might be used to advantage in ascertaining the temperature of the soil, we decided to undertake some experiments, not so much to obtain results that in themselves would be of value, but rather to find out the nature of the phenomena to be studied and to see if the thermophone was capable of throwing new light upon the subject.

A preliminary experiment was begun November 15, 1894. Two thermophone coils were placed in the ground under a lawn, one 6 and the other 7 inches deep. They were put near together in order to see what slight differences might be detected. Leading wires from these two coils were carried to an indicator in the house. From November 15 to November 22 observations were taken hourly during the day and evening. The results when tabulated and plotted brought out several interesting facts, the most important being the extreme sensitiveness of the instrument and the almost perfect smoothness of the curves. It was noticed that the temperature of the soil followed closely that of the air, the maximum for the day occurring a few hours after noon; the coil at 7 inches lagged behind the one 6 inches deep, and its range of temperature was not as great. One very interesting fact was noticed, namely, that when the surface of the ground became frozen the hourly fluctuations ceased.

A more extensive series of observations was begun November 24, 1894. A hole was dug in a lawn and horizontal borings made at depths of 4 inches, 1 foot, 2 feet, 3 feet, and 4 feet. The spot selected received the sun during the greater part of the day, being about 12 feet from the cellar wall on the south side of a house in Newton Centre, Massachusetts. The drifts were about 3 feet long and about $1\frac{1}{2}$ inches in diameter. A cylindrical temperature coil was located at the end of each of these drifts. In order that no heat might be conducted to or from the coils through the lead wires, a sufficient length of each lead was coiled in the ground at the same

depth as that of its coil, though not located at the same spot. The soil was the familiar bowlder clay overlaid with about 15 inches of loam. After the coils had been placed in position the hole was filled and grassed over. The three lead wires from each coil were carried

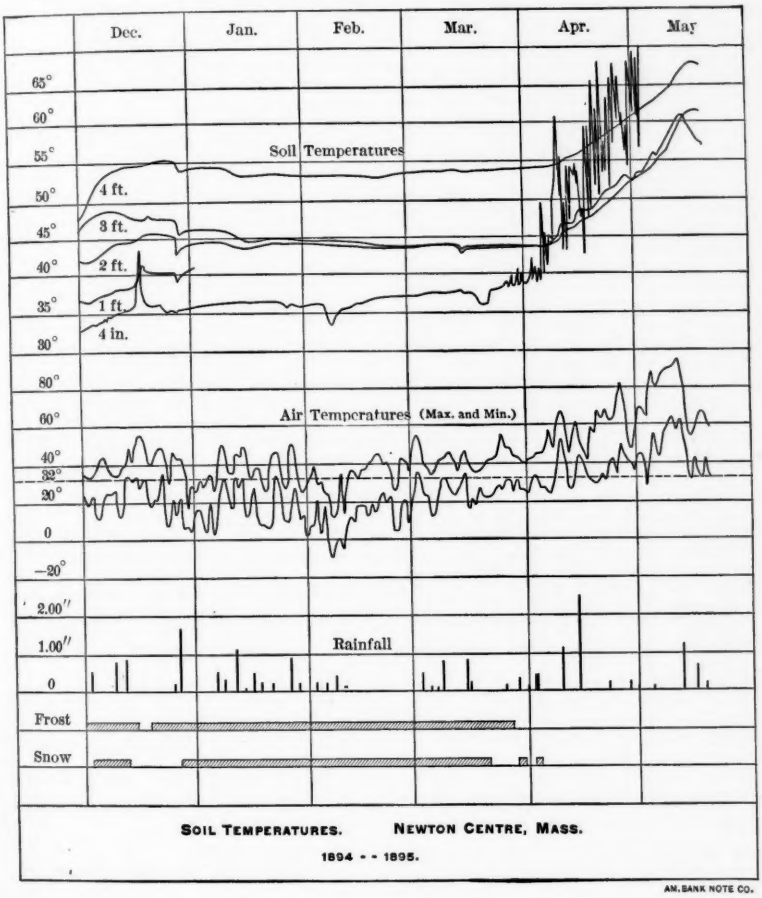

FIG. 11.

to a box at the surface, from which wires ran to a switchboard near the indicator in the house. By means of this switchboard one after another of the coils could be thrown into use and their temperature ascertained.

The general results of the observations, which have been taken from one to ten times each day, are shown in Figure 11, where the maximum and minimum air temperatures, the rainfall, etc., for the same period will also be found. On January 1 the coil 1 foot deep was thrown out of use by the breaking of one of the leading wires, caused by the settling of the ground. On May 3 the readings of the 4-inch coil went off the scale, which in the instrument used did not go above 70° F.

The curves bring out in a striking manner the fact noticed in the preliminary experiment, that when the ground is frozen there are no daily fluctuations in the temperature of the soil. The ground became frozen on the day after the coils were put in place, and it will be noticed that until December 16 the curves were quite smooth. Between December 16 and December 19 the weather was warm and the frost came out of the ground. During that time the curves showed considerable daily fluctuations. On December 19 the ground froze again, and remained frozen until March 27, after which daily fluctuations began again. It was a singular fact that throughout the winter, and in spite of the severe cold weather, the temperature at a depth of only 4 inches did not go below 33°. This was doubtless owing to the protection of the turf and to the covering of snow which remained on the ground during the greater portion of the winter; it is known that in exposed places the frost penetrated to a depth of several feet. On February 7 the temperature of the air went as low as 9° below zero, and, although the ground was covered with snow, there was a sudden drop in the temperature of the soil. It soon recovered, however, and continued to rise as long as the snow remained on the ground.

It was noticed that rain had a marked influence on the temperature. This was well shown on December 28, when, after a snow-storm which turned into a warm rain, the temperature of the soil, even to a depth of 4 feet, dropped rapidly on account of the infiltration of the cold water.

There are several things about the curves that we are unable to explain, such, for instance, as the reason why the 2 ft. and 3 ft. lines are so near together and the 4 ft. line so much higher. It should be remembered, however, that the location of the coils was far from ideal, and the temperatures were doubtless influenced by local causes of which we are ignorant.

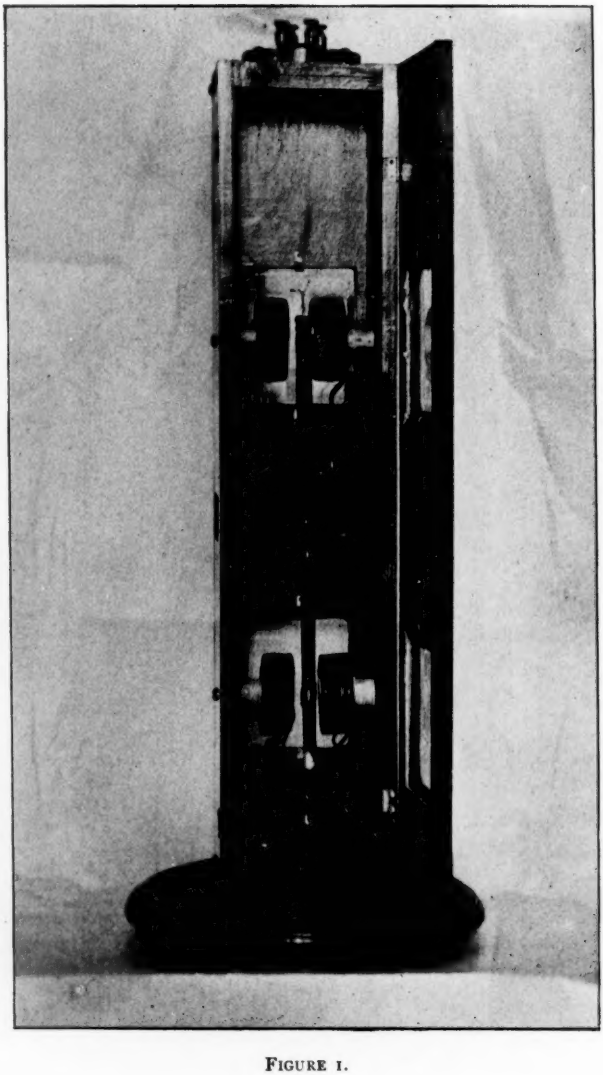

FIGURE 1.

EXPERIMENTS ON THE RELATION OF HYSTERESIS TO TEMPERATURE.[1]

By FRANK A. LAWS and HENRY E. WARREN.

Received May 11, 1895.

This paper gives an account of some experiments to determine the effect of temperatures much above the normal on the dissipation of energy by hysteresis in a specimen of steel.

At the time of the beginning of this research, in February, 1894, there were no complete studies of this subject known to us. A casual reference is to be found in the *Proceedings of the American Institute of Electrical Engineers*, VII, 325, 1890, by Professor Harris J. Ryan. The tests there referred to were made on a cast-iron ring. The maximum temperature employed was 360°. The details of the measurements are not given. A short paper by Dr. Wilhelm Kuntz appeared in the *Electrotechnische Zeitschrift*, 13, May 6, 1892. In this Dr. Kuntz showed that the hysteresis loss decreased with rise of temperature. A second paper by the same author appeared in the *Electrotechnische Zeitschrift*, 15, April 5, 1894. The magnetometer method was used by Dr. Kuntz in this work. In this paper tests of several ferrous materials are given, as well as some on a specimen of nickel.

At the outset of this research it was decided that alternating currents should be used and that the losses should be determined by a Wattmeter, thus reducing the time required for observations to a minimum. The instrument which we designed and used is shown in Figure 1. We have decided to call the arrangement a Watt-balance. Mr. A. E. Kennelly has given in the *Electrical Engineer*, December 21, 1892, a description of a "Differential Wattmeter." This instrument gives the difference of the mean values of two definite integrals representing the primary and secondary energy in a transformer, that is, the losses. The Watt-balance measures the ratio of the mean val-

[1] Read at a meeting of the American Academy of Arts and Sciences, October 10, 1894.

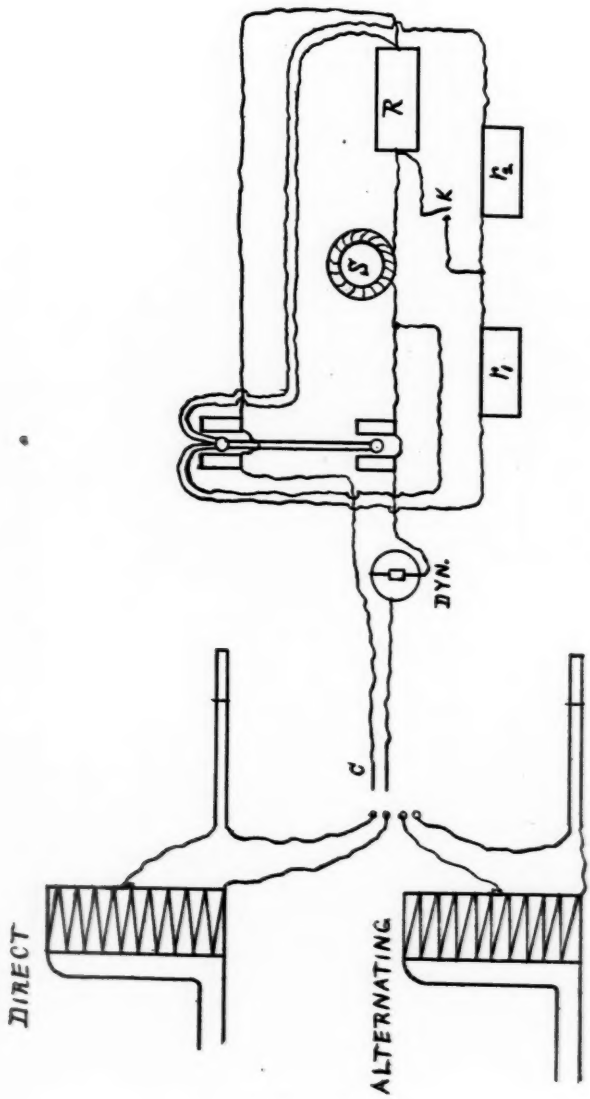

FIG. 2.

ues of two definite integrals. It can therefore be used to measure the efficiency of a convertor, giving the result by a single reading.

The Watt-balance consists of two electrodynamometer Wattmeters, one above the other. The movable coils are rigidly connected in our instrument by a spiral-wound paper tube, and consist of 100 turns of silk-covered German silver wire No. 32 B. & S. gauge. The resistance, including leads, is 103 ohms; the diameter of coils, 2 cm. In series with the movable coils are two adjustable resistances, r_1 and r_2, as shown in Figure 2. The stationary coils are arranged in pairs; each is 2.3 cm. in mean radius, and contains 130 turns of No. 12 cotton-covered wire. They are movable along their axes, so that the factor of the instrument may be adjusted. The vertical distance between the two dynamometers is 30 cm. The movable parts are suspended by a silk thread inside a narrow paper tube to prevent disturbance by air currents, and directive force is given by four spiral springs, made of copper wire 0.005 cm. in diameter. These springs serve as leading in wires for the movable coils. The instrument is read by a telescope and scale.

In Figure 2 is shown the scheme of connections for a hysteresis test. At the left the slide resistances for controlling the currents are shown. By the proper insertion of the connection, C, either a direct or an alternating current could be sent through the remainder of the apparatus, which in the main circuit consisted of an electrodynamometer, one pair of stationary coils, the specimen under test, a known resistance, R, of German silver strip immersed in kerosene oil to keep it at a constant temperature, and the second pair of fixed coils. At one terminal of R a connection was made by means of a short piece of stout wire and a key, K; beyond the key the circuit branched, passing through the adjustable resistances r_1 and r_2, the proper movable coils, and returning one lead to the external terminal of the specimen, and the other to the corresponding terminal of R. The resistance r_1 was some hundreds of ohms, seldom falling below 300, and was more frequently in the neighborhood of 1,000; r_2 was kept at a constant value, 976 ohms. The resistances r_1 and r_2 were ordinary plug boxes, and the assumption was made throughout the work that the resistances of circuits r_1 and r_2 were so high in comparison with their inductances that no correction factor need be applied to the indications of the Watt-balance. It may be well to mention that the use of high resistances constructed in the usual way by double winding may lead to

serious errors in alternating current measurements on account of the capacity effects.

If the plug C be inserted so that a current flows in the apparatus, and no deflection is observed, then the factors of the upper and lower dynamometers are equal; if the key K is depressed, there will in general be a deflection, which may be reduced to zero by adjusting r_1, as a zero reading means that the average values of the products of the currents in the two coils of the upper and lower dynamometers are the same. It is known that the work in S bears the same ratio to the work in R that the total resistance in circuit r_1 does to the total resistance in circuit r_2. If the current is alternating, the work in S is of course divided between hysteresis and heating losses. No allowance has been thought necessary for the work done in the suspended coils. If W_S and W_R represent the work in the specimen and in R, then

$$W_S = W_R \left(\frac{r_1 + 103}{r_2 + 103} \right) = \frac{I^2 R (r_1 + 103)}{r_2 + 103}.$$

I^2 is given by the electrodynamometer DYN.

To correct for the heating loss in S a direct current of any convenient magnitude is sent through the circuit, and a second balance, r_1^1, obtained.

$$R = 1{,}079 \text{ ohms}, \; r_2 = 976 \text{ ohms}; \text{ so } W_S = \frac{I^2}{1000} (r_1 - r_1^1).$$

It will be seen that the Watt-balance as used in the present case is a Wattmeter with an electrodynamic control. The advantage derived from obtaining this control by shunting a portion of the main current is that any manipulation of the circuits does not disturb the equilibrium of the instrument, and that it renders it possible to use the instrument in a null instead of a compensation method.

As the hysteresis loss is a function of the maximum magnetization, denoted by B, it was necessary to provide some means by which the maximum might be kept constant and its value determined. The device sketched in Figure 3 was used for this purpose. In addition to the magnetizing coil the specimen was provided with a winding of 24 turns, which was connected in series with an adjustable resistance of 874 ohms during the tests, and a galvanometer of 126 ohms. Leads were carried to the dynamo room, and terminated in brushes which rested on the edge of an ebonite disk 11 inches in diameter, fastened rigidly to the dynamo shaft; the brushes were carried by a radial arm,

the motion of which is controlled by a small magneto-motor driven by three Leclanche cells. The motor was governed by a reversing key in the testing room, about one hundred feet away. The alternator used had ten poles, thus making the length of a wave 72°. A piece of brass, 36° or one half a wave long, was set into the edge of the disk, and the whole carefully trued up. When the dynamo was in action the B current was closed once during a revolution and for a time corresponding to one half a wave length. The galvanometer then performs the operation

$$\frac{2}{T}\int_{t^1}^{t^1+\frac{T}{2}} C\,dt$$

fifteen hundred times a minute. The value of this integral will be a maximum when it extends over the time between $+B$ and $-B$. By

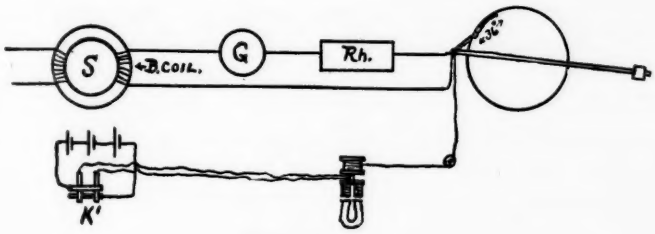

FIG. 3.

the use of the key K^1 the brushes may be shifted and the reading of the galvanometer brought to its greatest value. With the dynamo running at its normal speed a Leclanche cell, E. M. F. 1.4 volts, was inserted in the circuit; Rh was 1,374 ohms, and the deflection 21.2 cm.; with brushes short-circuited and Rh equal to 14,874 ohms the deflection was 21.8 cm., the ratio of deflection being .972. If the brushes made perfect contact, and there was no self-induction effect, the ratio would be unity, the entire cycle of operation being performed in a time short compared with the period of the galvanometer. During the tests the reading with $Rh = 1{,}374$ was frequently repeated in order that the brushes might be kept in as uniform a condition as possible.

Owing to the manner in which the specimen is constructed, the area included in the B winding is but partially occupied by the iron. In calculating the approximate values of B no allowance has been

made for this, as the permeability is high in the cases where B has been determined. If observations were taken at temperatures where the permeability was very low, it would be necessary to apply a correction for this unoccupied area. The values of B were calculated by the formula

$$B = \frac{E^1 R D}{20 A N n R^1 D^1}.$$

D is the deflection corresponding to the value of B to be found. R is the resistance in circuit Rh; N, the number of turns on B winding; n, the number of revolutions per second. A is the area of the iron included in the B windings. D^1 is the deflection of the galvanometer when an E. M. F. of magnitude E^1 and a resistance R^1 are inserted in the circuit Rh, the dynamo turning at the normal rate.

The furnace used for heating the specimen was built of fire-brick; the external diameter was about 36 inches, height 18 inches. Inside the fire-brick was a layer of asbestos wool $2\frac{1}{2}$ inches thick, kept in place by asbestos board, which was protected by thin sheet iron. The box containing the specimen was made of asbestos board about $1\frac{1}{2}$ inches in thickness, and lined with retort cement. During the tests it was tightly closed. The furnace was heated by three blast jets made of gas pipe; the external tubes were $\frac{3}{4}$ inch inside diameter, the inner tube $\frac{3}{8}$ inch. The supplies of gas and air were regulated by slide valves. The jets were directed into the furnace tangentially and with a slight upward inclination, the effect being to establish a good circulation and keep the interior of the furnace at a uniform temperature.

The specimen upon which the following tests were made was composed of so-called French steel, which showed on analysis the following impurities:

Manganese	0.535 per cent.
Phosphorus	0.013 per cent.
Silicon	0.085 per cent.
Sulphur	0.018 per cent.
Carbon	0.970 per cent.

The mass of iron employed was 628 grams. From this material, which was four one-thousandths of an inch thick, rings of 3 inches' outside and 2 inches' inside diameter were stamped, and the specimen formed by piling them. Each was insulated from its neighbors by a

layer of pipe clay, applied as a sort of paint, the clay having been moistened with alcohol. Every tenth layer was insulated with mica. The pile so formed was wrapped with asbestos cloth, and the magnetizing coil of 36 turns of No. 14 copper wire wound on. The wire was insulated by winding it with asbestos twine. Interwound with the magnetizing coil was the B coil of 24 turns. These two windings formed on the outside of the specimen a single layer. The temperatures were determined by a Le Chatelier pyrometer, calibrated by known melting points. The hot junction was placed inside the asbestos wrapping resting against the iron; the leads were brought out through the usual double-cored fire-clay tube; this was surrounded by a piece of gas pipe thoroughly wrapped in asbestos cloth, because in using this pyrometer in a case like the present, where the leads pass from the hot junction through a space at a higher temperature at a short distance from the junction, it is necessary to guard against conduction along the leads, and consequent errors in the temperature.

The manner of making the tests and the subsequent calculation was as follows: Owing to the construction of the furnace, the specimen being well shielded from the heat of the flames by the internal chamber, the air insulation, and its own asbestos covering, the temperature of the iron rises gradually; consequently the specimen will be at very nearly a uniform temperature. When a reading is desired the alternating current is turned on and the B deflection adjusted to its maximum value by K^1 and to its correct numerical value by varying the magnetizing current. Watt-balance resistance r_1 is now adjusted, and the pyrometer reading corrected for zero, and dynamometer reading and time observed; after a few minutes the observations are repeated, the temperature having risen in the mean time. This process is kept up until the iron loses its magnetism. Occasionally a direct current was sent through the apparatus, and the Watt-balance, dynamometer, and pyrometer readings taken; these allow the value of r_1^1 in the hysteresis formula to be determined by making a plot, the coördinates being Watt-balance and pyrometer readings; from the plot the value of r_1^1, corresponding to any pyrometer reading, may be read off. The electrodynamometers were calibrated by sending a direct current through them and measuring the *P. D.* at the terminals of a known resistance by projection against the E. M. F. of a Clark cell; the values of deflections and currents squared were plotted, giving straight lines. I^2 was determined by reference to these plots. The

zero errors of the dynamometers employed were very variable, and were determined after each reading.

The results of the measurements will now be given. They are plotted as referred to at the beginnings of the several tables.

TABLE I.

FIRST HEATING: ASCENDING CURVE.

(See Figure 4.)

$B = 1970$. $n = 125$. W_H = Hysteresis loss in specimen.

W_H.	Temperature. °	W_H.	Temperature. °
.852	23	.678	387
.834	45	.526	440
.845	67	.456	481
.845	98	.331	546
.817	132	.241	595
.809	181	.130	672
.818	272	.088	709
.742	347	....	....

The specimen lost its magnetic properties so rapidly that further measurements could not be taken on the ascending curve.

TABLE I.

DESCENDING.

W_H.	Temperature. °
.0	787
.161	576
.206	503
.255	445
.290	417

Power shut off.

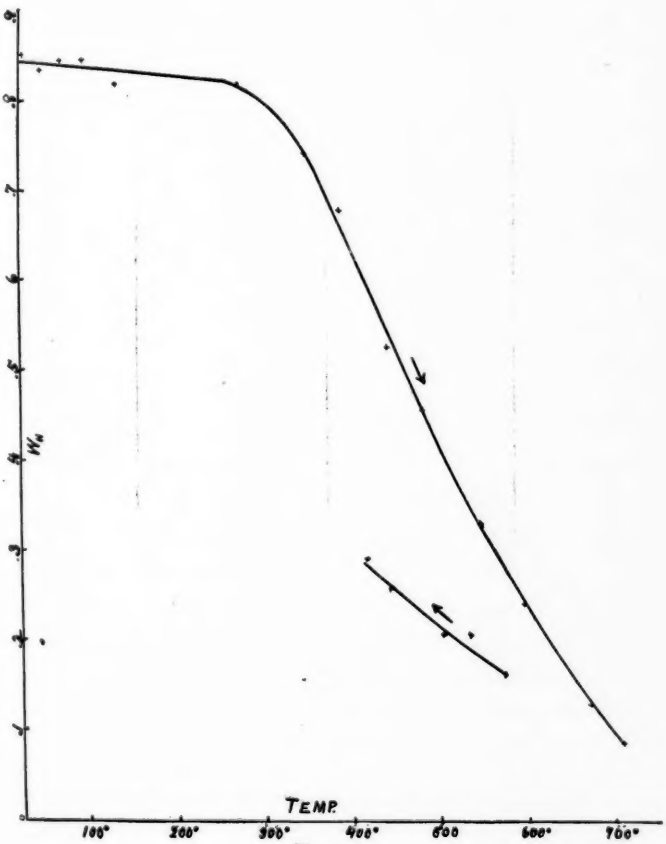

FIG. 4.

TABLE II.

SECOND HEATING: ASCENDING.

(See Figure 5.)

$B = 1974$. $n = 125$.

W_H.	Temperature. °	W_H.	Temperature. °
.516	20	.149	632
.520	75	.121	653
.519	108	.115	662
.522	160	.093	679
.440	269	.083	688
.407	310	.094	692
.378	345	.104	693
.340	397	.130	693
.321	423	.130	693
.311	438	.142	693
.293	470	.144	693
.258	511	.142	692
.228	555	.140	694
.167	593	....	....

Inspection of the plots shows (Figures 4 and 5) that for this sample of steel a moderate elevation of temperature up to about 270° has but a small influence on the hysteresis loss; that at this point a change takes place, and the diminution of hysteresis, with rise of temperature, is much more rapid, the decrease being such that at 675° the loss is but 13 per cent. of its value at ordinary temperatures. After heating above the inflection point, the specimen shows on cooling a marked decrease of the hysteresis loss from its value at the same temperature on the ascending curve. If the specimen be heated again, a change of direction of the curve takes place, but at a lower temperature. The second plot (Figure 5) shows an increase of the hysteresis loss after the point of inflection has been reached. As only two heatings were made, we were unable to verify these observations, the results of which became apparent only when they were reduced. In addition to the experiment at high temperatures, the following ob-

servations were made. A specimen was made up and the loss measured at the ordinary temperatures; a mean of three measurements gave .289 Watts as W_H. The specimen was then covered with a mixture of solid carbonic acid and ether; a mean of three measurements showed W_H as .288 Watts, showing that there is practically no change of hysteresis for a diminution of temperature to about — 80°.

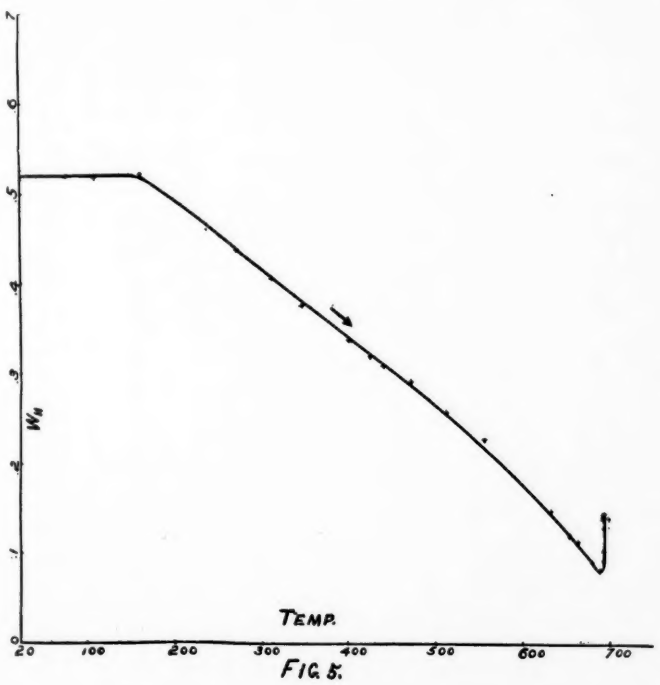

FIG. 5.

Between the ascending and descending observations of the second heating, readings were taken for the purpose of finding whether the temperature at which the iron becomes markedly magnetic on cooling is the same as that at which the sudden diminution of the magnetic properties occurs on heating. Simultaneous readings of the *B* galvanometer and pyrometer were taken, the current remaining constant, no adjustment for maximum was made. The readings, together with some from the descending curve of the first heating, are given below, and, after being corrected for zero, are plotted in Figure 6.

TABLE III.

First Heating.		Second Heating.	
B reading.	Pyrometer.	*B* reading.	Pyrometer.
38.8	7.17	28.1	6.99
38.8	7.10	29.9	7.01
38.8	7.05	31.0	7.02
38.8	7.00	32.1	7.03
38.7	6.95	33.4	7.05
38.55	6.90	34.8	7.10
38.15	6.83	36.1	7.11
37.70	6.80	37.2	7.12
37.00	6.73	37.9	7.13
36.3	6.69	38.3	7.14
33.65	6.51	38.6	7.15
31.2	6.45	38.7	7.15
....	....	38.6	7.19
....	....	38.8	7.14
....	....	38.75	7.10
....	....	38.75	7.03
....	....	38.7	7.01
....	....	38.65	6.98
....	....	38.55	6.95
....	....	38.25	6.93
....	....	37.85	6.90
....	....	37.1	6.85
....	....	36.5	6.84
....	....	34.1	6.76
....	....	32.7	6.73
....	....	30.7	6.70

Figure 6 shows that the two points do not coincide, that on the descending being about 12° lower than that on the ascending curve.

The difference of form of the curves is noticeable, showing that the regaining of magnetic properties on cooling is more gradual than their

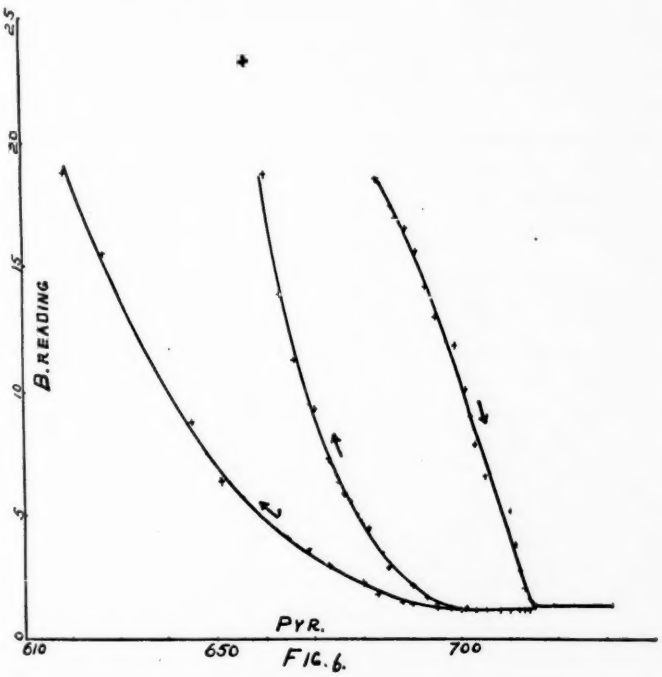

FIG. 6.

loss on heating; the sudden exaltation of magnetic properties occurs at the same temperature in the first and second coolings.

At the time of this writing the research has not been fully completed. We are, however, now engaged on further experiments, and hope to present additional data in the near future.

STUDIES ON THE VOLTAIC CELL. II.[1]

The Electrometric Determination of the Solubility of So-Called Insoluble Salts.

By H. M. GOODWIN, PH.D.

Received June 1, 1895.

The absolute potential difference between a metal and a liquid is, according to the modern osmotic theory of the voltaic cell, determined by a constant characteristic of the metal (its electrolytic solution pressure), and the partial osmotic pressure or concentration of the ions of the metal in the solution. This fundamental law has been deduced and shown in a previous paper[2] to be completely verified by a large number of experiments extended to elements in which the kathion concentration was varied between very wide limits. The exact expression for the potential difference of all reversible electrodes is

$$\pi = \frac{RT}{n_e \epsilon_0} ln \frac{P_M}{p}$$

$$= \frac{0.860}{n_e} T ln \frac{P_M}{p} \times 10^{-4} \text{ volt} \qquad (1)$$

where π is the *P. D.* between the metal and liquid, R the gas constant, T the absolute temperature, n_e the valence of the metal composing the electrode, ϵ_0 the quantity of electricity carried by each univalent ion, P_M the electrolytic solution pressure of the metal, and p the partial osmotic pressure of its ions in the solution.

The E. M. F. of any reversible element in which both electrodes are of the same metal is, therefore (neglecting the small *P. D.* at the junction of the liquids),

$$E = \frac{0.860\ T}{n_e} ln \frac{p_1}{p_2} \times 10^{-4} \text{ volt}, \qquad (2)$$

in which $\frac{p_1}{p_2}$ may evidently be taken as the ratio of the concentration

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[1] Translated and rewritten from Part III, "Studien zur Voltasche Ketten," Zeitschrift für Physikalische Chemie, **13**, 577, 1894.

[2] Technology Quarterly, **7**, 329, 1894.

of the kathions at the two electrodes. The validity of this formula having once been established, it is evident that, knowing the E. M. F. of the cell and the kathion concentration at one electrode, we can calculate the kathion concentration at the other. If this latter electrode is an electrode of the second kind, *i. e.*, a metal in a saturated solution of one of its salts (the *depolarizer*) in presence of a second soluble salt with identical anion, a determination of its kathion concentration leads to a determination of the actual solubility of the depolarizer.

The possibility of calculating the solubility of insoluble salts from electrometric measurements was first pointed out by Ostwald in 1892.[1] Conclusions regarding the relative solubility of a number of salts (mostly complex) have since been drawn by Zengelis[2] from the electromotive force of elements in which they were used as depolarizers, and Behrend[3] has applied the above theory to a method of electrometric analysis.

The following measurements are, however, the first which have been made with the view of actually determining the solubility of very difficultly soluble salts, so far as I am aware. The method is of particular interest since the appearance of the papers by Kohlrausch and Rose[4] and Holleman[5] in which measurements of the electrical conductivity of saturated solutions of difficultly soluble salts have been applied to the same end.

The form of element which first suggested itself as well suited to solubility determinations was the following, consisting of an electrode of the first and second kind:

Ag	x $AgNO_3$.	AgCl in x KCl	Ag.

The E. M. F. of this element is given by formula (2), in which p_1 is the concentration of the Ag-ions in the nitrate solution (equal to its concentration x multiplied by its dissociation), and p_2 is the concentration of Ag-ions in the chloride solution. This is determined by Nernst's second solubility principle, which, applied to the above case, requires that the product of the Ag- and Cl-ions shall under all conditions remain constant, that is, if p_2 is the concentration of the

[1] Ostwald, Lehrbuch, II (2d edition), 879.
[2] Zengelis, Zeitschrift für physikalische Chemie, **12**, 298, 1893.
[3] Behrend, ibid., **11**, 466, 1893.
[4] Kohlrausch and Rose, ibid., **12**, 324, 1893.
[5] Holleman, ibid., **12**, 125, 1893.

Ag-ions, and consequently, also, of the Cl-ions coming from the silver chloride, and p that of the Cl-ions coming from the potassium chloride, then

$$p_2 (p_2 + p) = s^2$$

where s is the solubility of silver chloride in pure water, its dissociation in this very dilute solution being assumed to be complete.

Since p_2 is evidently negligible compared with p, we obtain for p_2

$$p_2 = \frac{s^2}{p},$$

which substituted in (2) gives

$$E = 0.860\ T\ ln\ \frac{p_1 p}{s^2} \times 10^{-4} \text{ volt},$$

or

$$E = C\ ln\ \frac{p_1 p}{s^2},$$

where, for 25°, $C = 0.0256$.

Solving this equation for s we obtain

$$s = \frac{\sqrt{p_1 p}}{\sqrt{\phi}} \qquad (3)$$

where

$$\phi = e^{\frac{E}{C}}$$

Hence, knowing the concentration and dissociation of the silver nitrate and potassium chloride solutions and the E. M. F. of the cell, we can calculate the solubility of the depolarizer, silver chloride.

Although the above formula involves E as an exponent whereby a small error in the measurement of the electromotive force introduces a large error in s, yet from the peculiar form of the function it is easy to see that an error greater than 6 or 8 per cent. is in no case to be feared. For the error Δs in s produced by an error δE in E is

$$\Delta s = -\frac{s}{2C}\ \delta E,$$

or the percentage error is

$$\frac{100\ \Delta\ s}{s} = -\frac{100}{2C}\ \delta E,$$

that is, the percentage error in s is proportional to the absolute error in E. An error of 0.001 volt in the determination of the electromotive force at 25° would, therefore, introduce an error in s of

$$\frac{100 \times 0.001}{2 \times 0.0256} = 2\,\%$$

approximately, quite independent of the absolute value of E.

Since the experimental error in the measurement of the electromotive force of reversible cells of the above type is usually not greater than 0.001 — 0.002 volt, and under the worst conditions not greater than 0.004 volt, an error in the solubilities computed from them greater than 6 or 8 per cent. is not to be feared. An error of this magnitude, although large for most exact work, is not astonishing when the extreme minuteness of the solubilities in question is considered. A glance in any chemistry at the quoted solubilities of the so-called insoluble salts shows the great uncertainty with which they are known. Determinations by different investigators disagree often by multiples of each other, compared with which errors of even 8 or 10 per cent. fall into insignificance.

I have chosen as examples by which to illustrate the proposed method, the halogen silver salts. Their solubilities were determined at 25° from measurements of the E. M. F. of elements consisting of silver in silver nitrate, on the one hand, and silver, with an electrolytically deposited coating of silver chloride, bromide, or iodide in the corresponding halogen salt of potassium, on the other. The silver electrodes were in all cases first coated with a fine electrolytic deposit of silver to insure uniformity of surface. To obtain the best results the silver must be slowly deposited from a cyanide solution. To prevent the precipitation at the junction of the silver nitrate and halogen solutions a solution of potassium nitrate was interposed. The *P. D.* residing at the two resulting liquid junctions can easily be calculated by Planck's[1] formula for diffusion cells, and gives for the silver nitrate — potassium nitrate junction, 0.0023 volt from the former to the latter solution, and for the potassium nitrate — potassium chloride junction, 0.0009 volt in the reverse direction. The resulting *P. D.* of 0.0014 volt should, therefore, be subtracted from the total electromotive force of the cell to obtain the E. M. F. arising from the electrodes alone. As the *P. D.* of a diffusion cell is independent of its concentration, and as the velocity of migration of all halogen ions is practically the same, the above calculated correction is a constant for all of the cells investigated. I have, however, neglected to apply this correction in the following computations, as it falls within the limits of experimental error, which was found to amount to about 0.001 — 0.003 volt. To allow for it, however, one has only to increase the computed mean

[1] Wiedermann's Annalen, 40, 1890.

solubilities by $2 \times 1.4 = 2.8$ per cent., as we have seen an error of 0.001 volt produces about 2 per cent. change in the solubility. In all measurements the cells were immersed in a thermostat at 25° to insure constancy of temperature. The E. M. F. usually assumed a constant value within a few minutes after setting up the cells.

It was found by special experiments that within the experimental error the action of light had no effect on the electromotive force, so that no precautions were taken to prepare and keep the electrodes in the dark.

The results are given in the following tables: In the first column is the concentration of the solutions, experiments being made on cells of different concentrations to test the independence of the calculated solubility of the depolarizer of the nature of the cell. The observed values of the E. M. F. are given in the second column, and the solubility of the depolarizer computed by formula (3) in the third. The values of the dissociation of the nitrate and chloride solutions were computed from Kohlrausch's conductivity measurements. The solubility of the same salts as calculated by Kohlrausch and Rose, and by Holleman from measurements of the electrical conductivity of their saturated aqueous solutions, are also given. I have recalculated these at 25° for the chloride and bromide by Kohlrausch and Rose's formula

$$p_t = p_{18} \{ 1 + a (t - 18) \};$$

as the value of a for the iodide is not given, the recomputation of its solubility at 25° was impossible.

TABLE I.

Solubility of AgCl at 25°.

Concentration of $AgNO_3$ and KCl.	Observed E. M. F.	Solubility calculated by formula 3.
0.1	0.451	1.24×10^{-5}
...	0.449	1.28×10^{-5}
0.05	0.418	1.25×10^{-5}
...	0.419	1.23×10^{-5}
	Mean	1.25×10^{-5} at 25°
	Kohlrausch and Rose,	1.44×10^{-5} at 25°
	Holleman	1.81×10^{-5} at 26.5°

TABLE II.

Solubility of AgBr at 25°.

Concentration of $AgNO_3$ and KBr.	Observed E. M. F.	Solubility calculated by formula 3.
0.1	0.598	7.1×10^{-7}
...	0.603	6.4×10^{-7}
...	0.597	7.2×10^{-7}
0.05	0.570	6.4×10^{-7}
...	0.571	6.3×10^{-7}
...	0.570	6.4×10^{-7}

Mean . . . . . 6.6×10^{-7} at 25°

Kohlrausch and Rose, 20.9×10^{-7} at 25°

Holleman . . . . . 30.2×10^{-7} at 25°

TABLE III.

Solubility of AgI at 25°.

Concentration of $AgNO_3$ and KI.	Observed E. M. F.	Solubility calculated by formula 3.
0.1	0.815	1.02×10^{-8}
...	0.813	1.06×10^{-8}
0.05	0.815	1.02×10^{-8}
...	0.787	0.94×10^{-8}
...	0.786	0.96×10^{-8}
...	0.790	0.88×10^{-8}

Mean . . . . . 0.97×10^{-8} at 25°

Kohlrausch and Rose, 60.0×10^{-8} at 18°

Holleman . . . 395.0×10^{-8} at 28.4°

In the first place it is to be noticed that, as predicted, the solubility is independent of the concentration of the cell. This is particularly well verified in the case of the chloride, and sufficiently so in the other two cases. Also the decreasing solubility of the chloride, bro-

mide, and iodide inferred by Ostwald and Zengelis from E. M. F. measurements is completely confirmed.

A comparison of the actual solubilities with those obtained by the conductivity method is of still greater interest. The complete agreement of the results obtained for silver chloride by two such totally different methods leaves nothing to be desired. The difference between the results obtained by the two methods is, in fact, less than that between independent determinations by the same method. This agreement between the two methods lends great weight to the applicability of them both to solubility determinations of salts whose solubility lies in the region for which the methods are thus tested. In the case of the bromide and iodide, however, this agreement is not even approximately present. The solubility calculated by the conductivity method is three times as great as that calculated from electrometric measurements in the case of the bromide, and over sixty times as great in the case of the iodide.

The cause of this wide discrepancy is, I believe, to be found in the fact that absolutely pure preparations of the less soluble halogen salts, free from all traces of the precipitating agents, and particularly of traces of silver chloride, are probably impossible to prepare. The effect of such soluble or relatively soluble impurities, small as they may be, on the conductivity is evidently to increase it, the error thus introduced being greater the less soluble the salt investigated.

Thus any traces of the solutions from which the bromide, for example, was precipitated, or a trace of silver chloride, would go into solution before the bromide, and in the case of the iodide both chloride and bromide impurities would dissolve before the salt itself. When it is remembered that the conductivity of the water used by Kohlrausch and Rose was 1.0 to 2.0 referred to $Hg = 10^{10}$ as unity, and that it increased only 0.20 and 0.06 units when saturated at 18° with silver bromide and silver iodide, respectively, it is evident that even assuming absolute purity of the preparations we are working near the limit of applicability of the conductivity method itself.

On the other hand, slight impurities exert practically no influence on the E. M. F. of an element, for the halogen coated electrodes dip into solutions of potassium bromide or potassium iodide, whereby any more soluble silver salt present would instantly be changed over into the bromide or iodide, as the case might be. In the case of silver chloride, impurities of bromide or iodide would affect neither the conductivity nor E. M. F. to any appreciable extent, whereby the ex-

cellent agreement between the two methods for this salt is to be explained.

It should, moreover, be remembered that, whereas the accuracy of the conductivity method must necessarily diminish with diminishing solubility of the salt, this is not so in case of the electrometric method. As shown on page 168, the percentage error in the solubility is proportional to the absolute error in the E. M. F., which need not exceed 0.002 — 0.003 volt. Hence the accuracy of the method does not diminish with decreasing solubility; on the contrary, the formula (3) developed on page 168 holds more and more rigorously. It seems, therefore, that the electrometric method is unquestionably the more reliable for the determination of exceedingly small solubilities, say 0.1×10^{-5} and less, its value increasing with decreasing solubility and conversely. Unfortunately, it is limited in its applicability to salts of those metals which can be used as electrodes; thus the insoluble salts of the alkali earths cannot be investigated by this method.

On the other hand, the conductivity method is general and applicable to all salts. It is particularly convenient for determining the solubility of a salt at different temperatures. For salts whose solubility lies beyond the limit of exact analysis, say $1. \times 10^{-3}$ normal, and is less than, say $1. \times 10^{-5}$ normal, when the peculiar advantages of the electrometric method begin to be apparent, the conductivity method is undoubtedly to be preferred. Thus the two methods do not displace but supplement each other.

In order to compare both methods not only with each other but also with the analytical, the results of which could not be questioned, I determined the solubility of thallium bromide at 25° by all three methods. A saturated solution of the salt was prepared by rotating in a thermostat at 25° a solution containing an excess of the solid salt. After the undissolved salt had been allowed to settle, portions of the clear solution were titrated with a 0.1-normal silver nitrate and 0.02-normal potassium sulphocyanate solution, with iron alum as indicator. The conductivity of a second portion of the same solution was determined by the usual method at 25°. If the value of the molecular conductivity of thallium bromide at infinite dilution is assumed equal to that of thallium chloride, *i. e.*, $\mu_\infty = 140$ (an assumption undoubtedly correct, since Cl- and Br-ions have practically equal velocities of migration), and further that the bromide is completely dissociated, then s, the solubility, is

$$s = \frac{L}{140},$$

where L is the conductivity of the saturated solution in reciprocal ohms multiplied by the constant of the cell.

To determine s electrometrically, cells of the following type were used:

Tl amalgam	TlBr in x KNO_3	TlBr in x KBr	Tl amalgam,

as it was found that the E. M. F. of cells in which one electrolyte was thallium nitrate was very inconstant.[1] The above elements gave very constant values. The E. M. F. is evidently given by the formula

$$E = C\,ln\,\frac{s}{\frac{1}{2}\left(\sqrt{p^2 + 4s^2} - p\right)},$$

since, as already shown,[2] the number of Tl-ions in the potassium nitrate solution is practically the same as in a saturated aqueous solution. It is here assumed as before, that the bromide is completely dissociated.

Solving this equation for s we obtain

$$s = \frac{p\phi}{\phi^2 - 1},$$

where, as before,

$$\phi = \varepsilon^{\frac{E}{C}}$$

If ϕ^2 is large compared with 1, which is easily seen to be the case when $E > 0.06$ volt (when $\phi^2 = 100$, $E = 0.059$), we can put

$$s = \frac{p}{\phi}, \qquad (4)$$

by which formula s is calculated in the following table. This table contains in addition the results obtained by the analytical and conductivity methods:

TABLE IV.

Solubility of TlBr at 25°.

Concentration of KNO_3 and KBr.	Observed E. M. F.	s calculated by formula (4).	Conductivity of saturated TlBr solution.	s calculated from conductivity.	Analytical determination of s.
0.2	0.1149	0.00184	0.2780	0.00199	0.00202
0.1	0.1000	0.00175	0.2814	0.00201	0.00204

[1] Zeitschrift für physikalische Chemie, 13, 602.

[2] Technology Quarterly, 7, 343, 1894.

The excellent agreement between the last two columns proves the applicability of the conductivity method to moderately soluble salts. The wholly independent electrometric method leads to results about 10 per cent. lower. It must be remembered, however, that the method is here applied to a salt whose solubility lies outside the region in which its greatest accuracy is claimed to lie. The comparison of the three methods is nevertheless interesting.

Another form of element which would lend itself well to solubility determinations is that composed of two electrodes of the second kind, both of the same metal but of different depolarizers, *e.g.*, the element

Hg	HgCl in x KCl	HgBr in x KBr	Hg.

The electromotive force of this element is evidently given by the formula

$$E = 0.860\ T\ln\ \frac{p'}{p''} \times 10^{-4}\ \text{volt},$$

where

$$p' = \frac{s^2_{HgCl}}{p_1},\quad p'' = \frac{s^2_{HgBr}}{p_1}$$ (see page 168).

Substituting these values in the above equation,

$$E = 0.860\ T\ln\ \frac{s^2_{HgCl}}{s^2_{HgBr}} \times 10^{-4}\ \text{volt}. \qquad (5)$$

If the solubility of one of the depolarizers, *e.g.*, mercurous chloride, is known, that of the other can at once be calculated. Thus, assuming Kohlrausch and Rose's value 1.3×10^{-5} for the solubility of calomel at 18° and $E = 0.133$ volt, the value experimentally found for the above element at room temperature, we obtain for the solubility of mercurous bromide

$$s_{HgBr} = \frac{s_{HgCl}}{\sqrt{\phi}} = \frac{1.3 \times 10^{-5}}{\left(\frac{0.133}{\frac{0.0250}{\varepsilon}}\right)^{\frac{1}{2}}} = 9.1 \times 10^{-7}.$$

To determine the solubility of any other mercury salt we have simply to substitute it as depolarizer in place of the bromide, replacing at the same time the potassium bromide by a soluble salt with identical anion. In applying the above type of element to solubility determinations the solubility of at least one difficultly soluble salt must be known, to which the solubility of the others is referred.

This may be determined by one of the methods already mentioned, the one to be employed being determined by the solubility of the salt.

As the solubility of mercurous bromide has not been independently determined, formula (5) cannot be directly verified. I have verified it, however, completely for the exactly similar thallium element, the solubility of whose depolarizers was known by analysis beyond all question. The solubility of thallium chloride at 25° was found to be $s = 0.016$; that of thallium bromide, $s = 0.00203$. For 0.2-normal solutions of potassium chloride and potossium bromide it is easily shown that the conditions under which formula (5) was deduced are satisfied, and hence the E. M. F. of the element

Tl	TlCl in 0.2 KCl	TlBr in 0.2 KBr	Tl

is given by the formula

$$E = 0.860\ T\ ln\ \frac{s^2_{TlCl}}{s^2_{TlBr}} \times 10^{-4}\ \text{volt.} \qquad (6)$$

Remembering that the dissociation of TlCl in saturated solution at 25° is about 91.3, we obtain for the calculated E. M. F. of this cell $E = 0.1015$ volt, whereas it was actually found to be $E = 0.1013$ volt. A more complete confirmation of the formula and theory could not be desired.

One other interesting consequence of formula (5) should be mentioned. It follows at once from this formula that the E. M. F. is quite independent of the concentration of the potassium chloride and potassium bromide solutions. This consequence of the theory was found to be confirmed by experiment, as the following table shows:

TABLE V.

E. M. F. of HgCl-HgBr cells. 15° - 18°.

Concentration.	Observed E. M. F.
0.2	0.1336
0.1	0.1338
0.05	0.1335
0.01	0.1331
0.002	0.1323
0.001	0.1302

A similar series of experiments on the analogous thallium elements, however, gave only an approximately constant E. M. F., as will be seen from the following table:

TABLE VI.

E. M. F. of TlCl-TlBr cells. 25°.

Concentration of KCl and KBr.	Observed E. M. F.	Calculated E. M. F.
0.2	0.1013	0.1015
0.1	0.1007	.....
0.05	0.0991	.....
0.025	0.0958	.....

The observed and calculated values agree completely only for the most concentrated solution. The observed E. M. F. of the last three elements deviates more and more from that calculated by (6) as the concentration diminishes. This, however, is exactly what the theory requires in this case, as with diminishing concentration the condition under which formula (6) was deduced, namely, that the solubility of the depolarizer is negligible compared with the concentration of the electrolyte (or more precisely $\frac{s^2}{p^2} < 0.04$), becomes less and less exactly fulfilled. Deviations must, therefore, occur in the direction observed. The above series of experiments illustrates again what was established in the previous paper, that the theory and formulæ developed for so-called insoluble depolarizers are but limiting cases of the general theory of electrodes of the second kind applicable to depolarizers of any solubility.

The theory of the solubility method above explained and illustrated for binary salts may be extended without difficulty to ternary salts. This, however, as well as its further application to binary salts, must remain the subject for a future paper. My purpose in the present paper has been simply to explain and illustrate this new application of the osmotic theory of the voltaic cell — an application which in its turn furnishes additional evidence in support of this latest triumph of the osmotic theory of solutions and the theory of electrolytic dissociation.

ROGERS LABORATORY OF PHYSICS,
May, 1895.

SYNTHESIS OF DIPHENYLBIPHENYL AND ITS IDENTIFICATION AS BENZERYTHRENE.

BY ARTHUR A. NOYES AND ROLFE M. ELLIS.

Received June 4, 1895.

THE purpose of this investigation was to prepare synthetically the compound diphenylbiphenyl, C_6H_5-C_6H_4-C_6H_4-C_6H_5, and to determine by a comparison of its properties whether, as might be expected, it is one of the products of the action of heat on benzene. It seemed probable that this substance might be obtained by the Fittig reaction by the treatment of brombiphenyl with sodium, and accordingly an attempt was made to prepare it in this way.

Biphenyl was made in the usual manner by passing benzene through a red-hot tube. From this, brombiphenyl was prepared as described by Schultz.[1] It is to be noted that the body thus obtained is the para compound, since it yields parabrombenzoic acid on oxidation.[2]

Thirty grams of brombiphenyl were dissolved in three to four times the quantity of absolute ether, and an excess (5 grams) of thinly cut sodium added. The mixture soon heated to boiling, too violent action being prevented by surrounding the vessel with cold water. After two or three days the insoluble residue was separated from the ethereal solution by filtration. The solution was found to contain only unchanged brombiphenyl, and was used as the solvent for the brombiphenyl in the next sodium treatment. The residue was repeatedly extracted with hot water to remove the sodium bromide and excess of sodium. It was then dried and treated with successive quantities of cold benzene (200 cc. in all), which dissolved much the larger portion. By addition of alcohol to this benzene solution there was precipitated a brown flocculent substance insoluble in ether, chloroform, and petroleum ether, but very soluble in benzene and carbon bisulphide. All attempts to purify it by crystallization, sublimation,

[1] Annalen der Chemie, 174, 207.

[2] Ibid., 174, 209.

and distillation failed. The residue insoluble in benzene was of a dirty white color. It was found to sublime at a high temperature, and was purified between watch glasses in this manner.

The sublimate was pure white and in the form of large crystalline leaflets. It was proved to be pure diphenylbiphenyl by combustion and by a vapor density determination made by the Victor Meyer method in the vapor of boiling phosphorus pentasulphide (520°).

0.1364 gram substance gave 0.4684 gram CO_2 and 0.0735 gram H_2O.

0.1404 gram substance gave 11.70 cc. air measured over water at 27° and 759 mm.

	Calculated for $C_{24}H_{18}$.	Found.
C	94.12	93.65
H	5.88	5.99
Vapor density .	10.64	10.57

From the constitution of the brombiphenyl used, it follows that the phenyl groups must occupy the para positions with respect to the central bond. The yield obtained was in all cases very small, amounting only to 5 per cent. of the theoretical.

Several attempts were also made to prepare the body by the action of sodium on brombiphenyl in boiling benzene solution, but entirely without success. The product consisted wholly of the brown flocculent substance referred to above as being precipitated from the benzene extract by the addition of alcohol.

The melting point was accurately determined by heating portions of the substance inclosed in sealed capillary tubes in a flask in the vapor of boiling diphenylamine, the external pressure and consequently the boiling point being gradually increased until the substance liquefied. The temperature was then noted by means of a tested thermometer wholly immersed in the vapor. The melting point was found to be 317°.

The substance distilled without decomposition under a pressure of 18 mm. at 428° (roughly determined with a mercurial thermometer). Its behavior in the vapor density determination showed that its boiling point under ordinary pressure is below 520°, and that it is stable at that temperature.

The substance is completely insoluble in boiling alcohol, ether, chloroform, and carbon bisulphide, and in cold benzene. It was but very slightly soluble in boiling benzene, one part requiring more than two hundred parts of the solvent. It is of interest to compare these

properties with those of the isomeric substance, *s*-triphenylbenzene, which has been previously prepared by various investigators. The latter substance boils at 459° at 717 mm. (Crafts), melts at 170°, and is soluble in benzene.

It now remains to determine whether diphenylbiphenyl is produced by the action of heat on benzene. It is evident that it might result from a condensation of biphenyl in a manner similar to that by which this substance is formed from benzene.

A most thorough study of the high boiling hydrocarbons thus formed from benzene has been made by Schmidt and Schultz.[1] Of these the one which they named benzerythrene agrees closely in properties with our hydrocarbon, for the analysis of it corresponded to $C_{24}H_{18}$; it melted at 308°, boiled far above 360°, was insoluble in alcohol, and slightly soluble in boiling benzene, from which it crystallized on cooling. There is, therefore, no doubt that the two substances are identical, and consequently that paradiphenylbiphenyl is produced by the action of heat on benzene. It seems probable that this substance might be obtained in considerable quantity by passing biphenyl through a red-hot tube.

[1] Annalen der Chemie, **203**, 118.

REVIEW OF AMERICAN CHEMICAL RESEARCH.

ARTHUR A. NOYES, EDITOR.

ANALYTICAL CHEMISTRY.

Some Facts Observed in the Determination of Phosphoric Acid by the Molybdic Acid Process. BY RUDOLF DE ROODE. *J. Am. Chem. Soc.*, 17, 43–46. — The author finds that the precipitation of phosphoric acid as ammonium phospho-molybdate is complete after five minutes, at 65° C. He concludes, further, that the results of analyses as commonly conducted are too high, the error decreasing with increasing percentages of phosphoric acid. A re-solution and precipitation of the magnesium precipitate leads to correct results. No explanation is offered as to the source of this error, and desirable details of methods employed are lacking.

H. P. TALBOT.

The Addition of Calcium Chloride to the Solution of a Fertilizer in the Determination of Potash. BY RUDOLF DE ROODE. *J. Am. Chem. Soc.*, 17, 46–47. — The author criticises the suggestion of H. A. Huston, that calcium chloride should be added to a solution of a fertilizer in sufficient quantity to form tricalcium phosphate with all the phosphoric acid present, on the ground that the subsequent addition of ammonium oxalate, or carbonate, causes a portion of the phosphoric acid to pass into the filtrate from the precipitated calcium salts, unless the tricalcium phosphate precipitated by ammonia is removed by a separate and tedious filtration.

H. P. TALBOT.

On the Preparation of Ammonium Citrate Solution. BY RUDOLF DE ROODE. *J. Am. Chem. Soc.*, 17, 47. — A strictly neutral solution of ammonium citrate can be prepared, according to the author, by adding ammonia in slight excess to the warm solution, and allowing it to stand over night exposed to the air. The addition of 0.2 gram of salicylic acid per liter, before neutralization with ammonia, prevents the growth of fungus.

H. P. TALBOT.

The Determination of Potash in Manures. BY W. E. GARRIGUES. *J. Am. Chem. Soc.*, 17, 51–55. — The process involves (1) the ignition of the material with sulphuric acid, thereby converting all potash present to sulphate, if not already in that form, and at the same time expelling any ammonia and organic matter. (2) Precipitation of the sulphuric acid with barium chloride. (3) Precipitation of the excess of barium, together with the other earthy bases, by sodium carbonate. (4) Evaporation of the filtrate with platinic chloride as usual. Ten grams of the sample are cautiously mixed in a platinum dish with concentrated sulphuric acid and the mixture ignited, finally at a high heat, until the residue is white or red. The mass is trans-

ferred to a mortar, pulverized, triturated with hot water, and transferred to a 500 cc. graduated flask. It is boiled with 250 cc. of water for half an hour, and a 10 per cent. solution of barium chloride is added in portions of 5 cc., until no further precipitation is visible. A single drop of phenolphthalein solution is added, and sodium carbonate to a permanent rose color. The solution is then boiled for a minute, cooled, and made up to the mark. The precipitate is removed by filtration through a dry filter, and to 50 cc. of this filtrate hydrochloric acid is added to acid reaction, then platinic chloride, and the potassium is determined in the usual way. For the final weighing a Gooch crucible is employed. The results of analyses conducted by this method compare favorably with those obtained by the Lindo–Gladding and Stassfurt methods. The former of these methods the author finds unsatisfactory, the results being variable without apparent cause, and claims for his method greater efficiency and rapidity.

H. P. TALBOT.

The Determination of Potash in Kainite. BY RUDOLF DE ROODE. *J. Am. Chem. Soc.*, **17**, 85. — According to the author, the determination of potash can best be made by evaporation of the aqueous solution of the kainite with platinic chloride, with the usual subsequent treatment of the precipitated platinum salt.

H. P. TALBOT.

The Oxidation of Organic Matter and the Decomposition of Ammonium Salts by Aqua Regia, in lieu of Ignition, in the Determination of Potash in Fertilizers. BY RUDOLF DE ROODE. *J. Am. Chem. Soc.*, **17**, 86–87. — To avoid a possible loss of potassium during the ignition with sulphuric acid, or during direct ignition, it is suggested that the solution of the fertilizer be treated with aqua regia, which, it is claimed, destroys the ammonium salts, and either destroys the organic matter, or renders it harmless. The author is not prepared to give details of a complete method of analysis involving the use of aqua regia, and leaves one in doubt as to the positive value of his suggestion.

H. P. TALBOT.

The Determination of Nickel in Nickel Steel. BY E. D. CAMPBELL AND W. H. ANDREWS. *J. Am. Chem. Soc.*, **17**, 125–129. — The process described may be outlined as follows: One gram of the nickel steel is dissolved in a half-liter flask in 25 cc. of nitric acid (1.20), and the solution boiled until the nitric oxide is expelled. Thirteen grams of sodium pyrophosphate are dissolved separately in 75 cc. of warm water, but without boiling, and after filtration are added to the cooled solution of the steel, causing a heavy precipitate of ferric pyrophosphate. A 20 per cent. solution of sodium carbonate is then added until the precipitate has redissolved, an excess being carefully avoided. The solution is filtered through asbestos, and to the filtrate are added 2 grams of potassium xanthate dissolved in 25 cc. of water. This solution must be freshly prepared. The flask is stoppered and shaken at frequent intervals for ten minutes, after which the nickel will be completely precipitated as xanthate, together with any copper that may be in the steel, but almost free from iron, and wholly free from manganese. The precipitate is collected as rapidly as possible on an asbestos filter, and washed four or five times with a 1 per cent. solution of potassium xanthate, and subsequently dissolved in 20 cc. of freshly diluted fuming nitric acid, allowing the acid to drop

slowly on the precipitate. The filtrate is collected in a small Erlenmeyer flask, and the filter is washed first with hot water, then with 5 cc. of dilute sulphuric acid (2:3), and finally with more hot water. The solution in the flask is boiled rapidly until sulphuric anhydride fumes rise, cooled, diluted with 25 cc. of water, heated nearly to boiling, and the copper precipitated by sulphuretted hydrogen. The filtrate from the copper sulphide, containing the nickel and a small amount of iron, is boiled to expel the hydrogen sulphide, a few drops of hydrogen peroxide, or a few milligrams of sodium peroxide, added to oxidize the iron, and the latter precipitated by a slight excess of ammonia. This precipitate is redissolved in dilute sulphuric acid, and again thrown down by ammonia to free it from traces of nickel. The nickel in the filtrate may be determined electrolytically in the presence of 30 cc. of a 10 per cent. solution of disodium hydrogen phosphate and 25 cc. of strong ammonia, the nickel being precipitated on a platinum dish and washed with hot water and alcohol. A volumetric method for the determination of the nickel in the ammoniacal filtrate is also given, involving the use of potassium cyanide, a slight precipitate of silver iodide serving as indicator. The silver iodide dissolves as soon as the cyanide is present in excess. Directions are given for the preparation of the standard solutions. The results of analyses by both methods, as presented, are satisfactory.

H. P. TALBOT.

The Volumetric Determination of Phosphorus in Steel and Cast Iron. BY W. A. NOYES AND J. S. ROYSE. *J. Am. Chem. Soc.*, **17**, 129–137. — In a previous paper by W. A. Noyes and E. D. Frohman (*J. Am. Chem. Soc.*, **16**, 553) it was shown that in the reduction of molybdic solutions by the Jones' reductor the molybdenum is reduced to Mo_2O_3, and that the reduced solution is very easily oxidized upon exposure to the air. The authors were led to suppose that this would account for the difference between the theoretical factor for the calculation of the phosphorus equivalent of a permanganate solution from its iron equivalent, and the empirical factor given by Dudley and Pease (*J. Am. Chem. Soc.*, **16**, 230). This statement was questioned, and a repetition of the work seemed to show that while the factor named by Dudley and Pease gives results nearly or quite correct for steels containing 0.03 to 0.04 per cent. of phosphorus, it fails if the amount present falls either above or below these limits. This is apparently due to the incomplete precipitation of the phosphorus under the prevailing conditions, when the amount present is less than 0.05 per cent., and to the co-precipitation of free molybdic anhydride when the amount of the phosphorus is greater. These considerations led to the modification of the process in order to secure the complete precipitation of small amounts of phosphorus, and also to secure the precipitation of a definite compound regardless of the amount present. The process finally determined upon is the following: Two grams of steel are dissolved in 50 cc. of nitric acid (1.18) with only gentle warming, until solution is complete, to avoid a possible loss of phosphorus if the gases become colorless before solution ensues. The solution is then boiled for one minute, 10 cc. of a permanganate solution (12.5 grams per liter) are added, and the boiling continued until the pink disappears, after which ferrous sulphate is cautiously added until the solution clears. The temperature is reduced to 50°, 8 cc. of ammonia (0.90) are added, and the stoppered flask shaken until the precipitate formed redissolves. It is then cooled, or heated, until the solution is as many degrees above or below 60° as the molybdic solution is above or below 27°,

60 cc. of molybdic solution are added, and the stoppered flask is shaken for five minutes. After settling for five minutes, the precipitate is filtered and washed with acid ammonium sulphate solution, using 5–10 cc. at a time When 5 cc. of the wash water fail to give a brown with dilute sulphuretted hydrogen water, the precipitate is dissolved in dilute ammonia (12 cc. ammonia (0.96) diluted to 25 cc.), the filter washed with 100 cc. of water, the filtrate further diluted with 80 cc. of water, and 10 cc. of concentrated sulphuric acid are added. The solution is then passed through a Jones' reductor, followed by 200 cc. of water, without allowing any air to pass through during filtration or washing. This filtrate is titrated immediately with potassium permanganate. For steels high in phosphorus an aliquot portion of the ammoniacal solution is taken. Cast irons may require more ammonia to dissolve the precipitate. — The molybdic solution is made up from 100 grams of molybdic anhydride, 400 cc. of ammonia (0.96), and 1,000 cc. nitric acid (1.20). To this 1 cc. of a 10 per cent. solution of sodium phosphate is added, and the resulting precipitate removed by filtration. This solution is stable.— The permanganate solution for titration contains 2 grams per liter. — The results of analyses seem to indicate that this procedure furnishes the desired conditions for a precipitate of constant composition. They agree with those obtained by careful gravimetric analysis. The presence of arsenic and silicon is without influence upon this determination, if carried out as described.

H. P. Talbot.

The Determination of Phosphoric Acid. By H. Pemberton, Jr. *J. Am. Chem. Soc.*, **17**, 178–181. — The suggestions offered in this paper refer to the procedure involving the alkalimetric titration of the yellow precipitate. The author points out that phenolphthalein should be used as indicator in standardization, as well as in the determination, to avoid errors arising from the presence of aluminates and carbonates in the caustic hydrate. He notes further that under the prescribed conditions (*J. Am. Chem. Soc.*, **15**, 387) the successive addition of three portions, of 5 cc. each, of the molybdic solution will just reduce the temperature to 70°, the desired point, and suggests that the washing of the precipitate is promoted if the molybdic solution be allowed to run slowly into the liquid with frequent stirring. The filtration is best accomplished on a small Hirsch porcelain funnel, or a porcelain disk covered with paper. Certain other modifications are briefly mentioned, the details of which may be found in the report of the Association of Official Agricultural Chemists for 1894.

H. P. Talbot.

On the Estimation of Sulphur in Pyrites. By G. Lunge. *J. Am. Chem. Soc.*, **17**, 181–187. — The author criticises a paper published by T. S. Gladding (*J. Am. Chem. Soc.*, **16**, 398) under the same title, in which are proposed certain modifications of Lunge's method, as published in his *Alkali-makers' Handbook*. He claims that the decomposition of the pyrites by nitric acid and bromine, as proposed by Gladding, is more tedious than by a mixture of nitric and hydrochloric acids, though the former is finally effective. He also claims that it is possible to wash the precipitated ferric hydrate free from all traces of sulphate if his directions are followed, and that Gladding's procedure, which includes the re-solution of the precipitate and attempted precipitation of the small amount of sulphate present by means of barium in the ferric chloride solution, is inaccurate, and furnishes certain data to sustain his

statement. He finds that the only satisfactory procedure for the detection of sulphate in the ferric hydrate precipitate includes fusion with sodium carbonate, and precipitation with barium chloride from the aqueous extraction of the fusion after proper acidification. Professor Lunge criticises Gladding's procedure in the precipitation of the barium sulphate as consuming unnecessary time, and claims that no barium chloride is carried down with the sulphate if his own directions are followed. — The method of F. Johnson (*Chem. News*, 70, 212), involving the reduction of the iron by sodium hypophosphite, has shown itself to be unreliable in Professor Lunge's hands.

H. P. TALBOT.

The Superiority of Barium Hydroxide Solution as an Absorbent in Carbon Determinations in Steel. BY JAMES O. HANDY. *J. Am. Chem. Soc.*, 17, 247–251. — It is claimed for the use of barium hydroxide solution as an absorbent in carbon determinations (with subsequent titration for the unprecipitated barium), that the errors arising from changes of temperature and humidity, which so easily affect the determination when the Geissler potash bulb is used, are excluded by this method. The carbonic acid from the combustion tube is passed over calcium chloride and anhydrous copper sulphate, and is then allowed to bubble through a measured quantity of barium hydrate solution in long tubes, a sketch of which is given in the original article. The precipitated carbonate is filtered off, with precaution to prevent precipitation by the carbonic acid of the atmosphere, and the unused barium hydroxide is determined by titration of the filtrate with decinormal sulphuric acid, the indicator being phenolphthalein. For details concerning necessary precautions and the preparation of solutions, reference is made to the original paper.

H. P. TALBOT.

Note on the Estimation of Iron and Alumina in Phosphates. BY K. P. MCELROY. *J. Am. Chem. Soc.*, 17, 260–263. — The author calls attention to the fact that the method for the estimation of iron and alumina, which is sometimes called by his name, though really an adaptation of a process given in *Crookes' Select Methods*, page 538, may sometimes yield erroneous results. The procedure involves the precipitation of the hydroxides in the presence of an excess of ammonium molybdate, and it has been found that molybdic acid and calcium, if present, are easily carried down with the hydrates of iron and alumina, while, on the other hand, the precipitation of the alumina is incomplete.

H. P. TALBOT.

Estimation of Tellurium in Copper Bullion. BY CABELL WHITEHEAD. *J. Am. Chem. Soc.*, 17, 280–281. — To a solution of 25–50 grams of the bullion in nitric acid, 32° B., from which the excess of acid has been removed by boiling, an amount of ferric nitrate solution containing 0.25 gram of iron is added. Ammonia is added in excess to the hot solution, and the copper is removed from the precipitate by washing with dilute ammonia water and by reprecipitation, if necessary. The precipitated ferric tellurite and selenite is dissolved in hydrochloric acid, tartaric acid is added in excess, and, after making alkaline with caustic potash, hydrogen sulphide is passed into the solution, converting the selenium and tellurium to soluble sulphides. After filtration the alkaline sulphide is destroyed with dilute hydrochloric acid, the sulphuretted hydrogen removed by allowing the solution to stand in

a warm place, and the solution again filtered. The sulphides of selenium and tellurium are dissolved in aqua regia, the solution taken to dryness, the residue dissolved in hydrochloric acid, and the two metals precipitated by sulphurous acid added to saturation. After standing twelve hours in a warm place the precipitate is filtered on a tared filter, and weighed at 100°. The selenium is separated from the tellurium by boiling the precipitate with concentrated potassium cyanide solution, filtration, and precipitation of the selenium from the filtrate by hydrochloric acid, as a brick-red precipitate, which is dried at 100° and weighed. The tellurium is determined either by difference, or the small quantity dissolved may be precipitated from the cyanide solution by sulphurous acid and collected with the portion insoluble in the cyanide, and weighed.

H. P. TALBOT.

Note on the Determination of Zinc. BY P. W. SHIMER. *J. Am. Chem. Soc.*, **17**, 310–312. — To avoid the double precipitation of zinc sulphide, which is necessary when the zinc is precipitated in that form in the presence of manganese, the author throws down the manganese from a nitric acid solution by means of potassium chlorate (Ford's method), and removes the oxide by filtration through purified asbestos. A double basic acetate separation of zinc from iron and aluminum is made in the filtrate and the zinc precipitated as sulphide from a boiling solution. This zinc sulphide is redissolved in hydrochloric acid and the zinc precipitated as zinc ammonium phosphate. The latter should be ignited at a low, red heat to avoid fusion of the precipitate. The manganese precipitate contains some iron, but no appreciable quantity of zinc.

H. P. TALBOT.

Method of Determining Chromium in Chrome Ore. BY EDMUND CLARK. *J. Am. Chem. Soc.*, **17**, 327–330. — The chrome ore is first fused in a large platinum crucible, with potassium bisulphate, and the fused mass is boiled with water and hydrochloric acid until only silica remains undissolved, which is separated and weighed. The iron, alumina, and chromium are twice thrown down as hydrates with ammonia, and the lime and magnesia determined in the filtrate. The hydrates are dissolved in nitric acid (sp. gr. 1.42), and potassium chlorate is added until the chromium is wholly oxidized to chromic acid, as indicated by the color, after which the iron and alumina are again precipitated as hydrates and determined. The chromium is once more reduced by sulphurous acid and precipitated by ammonia in the form of hydrate, and ultimately weighed as oxide. Detailed directions and precautions are given in the original article. As an alternative method for the determination of the chromium is proposed the precipitation of the chromic acid, in the form of lead chromate, from the filtrate containing the ammonium chromate, after acidulating with acetic acid, the lead chromate to be weighed on a tared filter at 100° C. It is proposed in a later article to deal with the method as applied to chrome steel and ferro-chrome.

H. P. TALBOT.

Methods for the Determination of Manganese. BY W. S. THOMAS. *J. Am. Chem. Soc.*, **17**, 341–346. — The author has attempted a critical study of Low's and Volhard's methods for rapid manganese determinations, from which it would appear that the former method was not reliable, while the lat-

ter (as has long been known) yields technically satisfactory results. Many of the statements in the paper are confused and obscure, and others are based upon an entire misconception of the principles of stochiometry.

H. P. TALBOT.

The Wet Assay for Copper. BY R. S. DULIN. *J. Am. Chem. Soc.*, 17, 346–351. — The author has made a critical study of the cyanide, iodide, and electrolytic methods for the determination of copper. He notes that in the cyanide method care must be taken that the volume of the solution shall be uniform, that the solution shall be at laboratory temperature, and that a definite quantity of ammonia shall be added. Manganese, calcium, zinc, and cadmium interfere with the determination as usually conducted. The author recommends the previous precipitation of the copper by means of aluminum foil, separation from the solution, and re-solution in nitric acid. It is claimed that by this procedure the process gains accuracy and the copper is separated from other metals likely to interfere. The same modification is recommended in the iodide and electrolytic methods. Both the latter methods require a longer time for completion than the cyanide method, and the iodide method generally yields results from 0.1–0.3 per cent. too high.

H. P. TALBOT.

On the Standardization of Sulphuric Acid. BY F. S. SHIVER. *J. Am. Chem. Soc.*, 17, 351–354. — Weinig has recommended as a desirable method for the standardization of sulphuric acid solutions (*J. Chem. Soc.*, 64, 145) the conversion of the acid into ammonium sulphate and the weighing of the latter after drying at 110°–120°. The author finds that it is necessary to moisten the ammonium sulphate with ammonia, and to evaporate a second time to compensate for a slight loss of ammonia occurring during evaporation. The results of this method agree with the barium sulphate method.

H. P. TALBOT.

The Determination of Sulphur in Pyrites. BY T. S. GLADDING. *J. Am. Chem. Soc.*, 17, 397–402. — In this paper Mr. Gladding replies to Lunge's criticisms (this *Quart.*, 8, 184) of his modification of the latter's process, reaffirming his previous statements. He furnishes data to show that unless the barium chloride be added drop by drop the barium sulphate occludes some chloride, and also to show that in the presence of an excess of barium chloride the barium sulphate is not "very seriously" soluble in hot acid solutions of ferric chloride. For the details of the discussion reference must be made to the original paper.

H. P. TALBOT.

The Zimmermann-Reinhardt Method for the Determination of Iron in Iron Ores. BY C. T. MIXER AND H. W. DUBOIS. *J. Am. Chem. Soc.*, 17, 405–411. — The procedure described is that in use in the Lake Superior iron region. About 0.5 gram of the ore is treated with 2.5 cc. of a solution of stannous chloride (made by dissolving 500 grams of the chloride in 500 grams of hydrochloric acid (1.2) and diluting to two liters) and 10–15 cc. hydrochloric acid (1.1). Solution ensues very promptly. To the hot solution additional stannous chloride is added from a burette until the iron is just reduced. If an excess be already present it is oxidized with a few drops

of permanganate and then brought to the desired point. To this solution 5 cc. of a saturated mercuric chloride solution are added, and the whole is washed into a large beaker containing 400 cc. of water and 6–8 cc. of a solution made by dissolving 160 grams of manganous sulphate in 1750 cc. of water, to which 330 cc. of phosphoric acid (1.7 sp. gr.) and 320 cc. of sulphuric acid (1.84) have been added. The iron is then titrated with a potassium permanganate solution which has been standardized under the same conditions. It is claimed for this procedure that it is simple, rapid, and accurate.

H. P. TALBOT.

On Some Conditions Affecting the Accuracy of the Determination of Potash as Potassium Platinichloride. BY A. L. WINTON. *J. Am. Chem. Soc.*, **17**, 453–466. — The author finds that potassium platinichloride is precipitated in the form of larger crystals when the platinum salt is added to a solution of potassium chloride containing not over 1 gram to 100 cc., with subsequent evaporation, than when it is added to a more concentrated solution. The larger crystals are seen under the microscope to contain but few cavities inclosing mother liquor, while in the finer crystals such cavities are numerous. The results are always slightly too high when the potassium chloride solution is concentrated before the addition of the platinum solution. The presence of sodium and magnesium salts leads to low results whatever the dilution. A method based upon precipitation in dilute solution, with subsequent evaporation, drying the precipitate at 100° and the use of the factors 0.30688 for potassium chloride and 0.1939 for potassium oxide (based upon the latest atomic weight determinations), gave satisfactory results.

H. P. TALBOT.

The Indirect Analysis of Mixtures Containing a Common Constituent. BY EDWARD K. LANDIS. *J. Am. Chem. Soc.*, **17**, 466–468. — The paper relates only to methods commonly in use for the calculation of indirect analyses, and offers nothing new.

H. P. TALBOT.

The Volumetric Determination of Zinc and a New Indicator for Ferrocyanide. BY GEORGE C. STONE. *J. Am. Chem. Soc.*, **17**, 473–477. — The author describes a method in use in the New Jersey Zinc and Iron Company's laboratory for the determination of zinc. The ore is brought into solution by means of hydrochloric acid and potassium chlorate, or by fusion if required, copper and lead are thrown down by aluminum (lead alone need not be removed), cadmium by sulphuretted hydrogen, and iron and alumina by barium carbonate free from all impurities. In a portion of the filtrate from the barium carbonate precipitate the manganese is determined by titration with potassium permanganate. In another portion the manganese and zinc are determined together by means of potassium ferrocyanide, using cobalt nitrate as an indicator. Before titration hydrochloric acid (5 cc. concentrated acid to 100 cc. of solution) is added. The end-point is reached when a drop of the liquid brought into contact (not mixed) with a drop of a dilute solution of cobalt nitrate on a porcelain plate causes an immediate, faint greenish line at the point of contact. A blank analysis must be made to determine the amount of the ferrocyanide solution required to

above. The acid prepared by this method was found to contain 0.9831 grams per cubic centimeter, and the procedure need not occupy more than two days. — The determination of potassium was carried out as follows: The solution, free from sulphuric acid, was freed from hydrochloric acid by evaporation, the residue stirred with 20 cc. of hot water, and one and one half times the amount of perchloric acid required by the bases added. It is repeatedly evaporated until fumes of the perchloric acid appear, to remove traces of hydrochloric acid. The residue is treated repeatedly with 97 per cent. alcohol, containing 0.2 per cent. of pure perchloric acid, and finally weighed on a Gooch crucible at 130°. If phosphoric acid be present, a considerable excess of perchloric acid must be used before the alcohol treatment.

H. P. Talbot.

Barium Hydrate as an Absorbent in Carbon Determinations. By A. G. McKenna. *Proc. Engineers' Soc., Western Pa.*, **11**, 105–109. — This paper does not differ essentially from that by G. O. Handy (this *Quart.*, **8**, 185).

H. P. Talbot.

Method of Determining Chloride in Ammonium Chloride. By C. B. Dudley and F. N. Pease. *Am. Eng. R. R. J.*, **49**, 33. — The conditions essential for the titration of the chlorine by silver nitrate, with potassium chromate as indicator, are carefully described in this paper.

H. P. Talbot.

Method of Determining Ammonia in Ammonium Chloride. By C. B. Dudley and F. N. Pease. *Am. Eng. R. R. J.*, **49**, 72–75. — This paper presents a detailed description of the determination of ammonia by distillation, absorption of the ammonia in acid, and titration of the excess of acid, with all the necessary precautions.

H. P. Talbot.

Sugar-Ash Analysis. By F. G. Wiechmann. *School Mines Quart.*, **16**, 128–134. — The author gives in detail a method for the determination of the carbonate ash, embodying some alterations in the scheme previously proposed by him (*School Mines Quart.*, **11**, 15). He proposes that all constituents determined be recorded as elements and that the report state the method of determination.

C. W. Andrews.

Inorganic Chemistry.

Some of the Properties of Calcium Carbide. By F. P. Venable and Thomas Clarke. *J. Am. Chem. Soc.*, **17**, 306–310. — The calcium carbide is made by heating together lime and some form of carbon — generally coal tar — until a uniform mixture results, which is in turn subjected to the heat of an electric furnace. The fused mass comprises unchanged carbon (graphitic) and the calcium carbide. They are easily distinguished in appearance, but no satisfactory method for their mechanical separation could be found. The masses of calcium carbide are dark brown, lustrous and hard, and break with crystalline fracture. They lose their luster on exposure to air, more rapidly if the air be moist, and disintegrate to a gray powder, with

show an end-point with the volume of liquid used. The composition of the manganese precipitate is not normal, but is $Mn_3[Fe(CN)_6]_2$. It is well to make a preliminary titration unless the quantities of zinc and manganese are approximately known. The zinc is determined by difference, and the results are technically satisfactory. For details regarding solutions the original paper must be consulted.

H. P. TALBOT.

Separation of Nickel and Iron. BY E. D. CAMPBELL AND W. H. ANDREWS. *Am. Chem. J.*, **17**, 164–167. — This paper is essentially the same as that by the same authors published under the title "The Determination of Nickel in Nickel Steel" (this *Quart.*, **8**, 182).

H. P. TALBOT.

On a New Method for the Separation of Copper and Cadmium in Qualitative Analysis. BY ALLERTON S. CUSHMAN. *Am. Chem. J.*, **17**, 379–383. — Cadmium sulphide is found to be readily soluble in saturated solutions of the alkali chlorides containing small amounts of hydrochloric acid, probably with the formation of double salts. The alkali chlorides alone fail to exert this solvent action. The separation of copper and cadmium can be effected as follows: About 2 cc. of the solution of the two metals is made slightly acid with hydrochloric acid, and about 20 cc. of a saturated solution of sodium chloride is added, the solution warmed and hydrogen sulphide passed through until the copper is precipitated. The copper sulphide is quickly filtered on a *dry* filter and into a dry test tube. If a few drops of water are allowed to run down the sides of the tube a yellow ring is formed at the junction of the water and solution if cadmium be present, or dilute ammonia may be used, which develops the ring more quickly, but may throw down other metals not completely removed. Lead and bismuth must be carefully excluded, as their sulphides are soluble with the cadmium sulphide. This procedure has been found to be very satisfactory.

H. P. TALBOT.

The Preparation of Perchloric Acid and its Application to the Determination of Potassium. BY D. ALBERT KREIDER. *Am. J. Sci.*, **49**, 443–448. — The preparation of perchloric acid from sodium chlorate is described as follows: From 100–300 grams of the chlorate are melted in a glass retort or round-bottomed flask and the temperature gradually raised until the fused mass thickens throughout. The product is washed from the retort and treated with hydrochloric acid until the residue of the chlorate is destroyed, and the solution evaporated to dryness. The residue, consisting of sodium chloride and perchlorate, is triturated with an excess of concentrated hydrochloric acid, the acid decanted, and the operation repeated. The supernatant liquid is filtered through a Gooch filter; the sodium chloride, which remains insoluble, is finally thrown on the filter and washed with strong acid. The filtrate is evaporated to expel the hydrochloric acid and until the fumes of perchloric acid appear, when it is ready for use in potassium determinations. A small quantity of sodium is present, but in the form of perchlorate, which is soluble in 97 per cent. alcohol, and therefore harmless. If potassium be present in the sodium perchlorate, or introduced from vessels, the mixture of sodium perchlorate and chloride, after treatment with hydrochloric acid, must be extracted with 97 per cent. alcohol, which dissolves only the sodium perchlorate. The alcohol is removed by distillation and the residue treated as

particles of graphite through it. It may be kept for some time out of contact with the air, best under petroleum. The carbide is easily decomposed by water with the evolution of acetylene. The gas is entirely absorbed by an ammoniacal copper solution. The average quantity of gas is 200 cc. per gram of the carbide, the amount varying with the amount of graphite present. No satisfactory analyses were obtainable, owing to the presence of impurities. Moissan gives CaC_2 as the symbol. The behavior of the carbide toward various reagents has been studied, with the following results: Dry hydrogen has no action in the cold, and after heating for five hours in an atmosphere of hydrogen no change other than the expulsion of the tarry matter was noticeable. Dry air is without effect upon the carbide even when heated, and oxygen only attacks it slowly at very high temperatures. When heated in an atmosphere of hydrochloric acid the substance swells up to a gray mass and calcium chloride is formed, while in an atmosphere of chlorine the carbide glows brightly and fuses. Much of the carbide is undecomposed. In an atmosphere of bromine and air calcium bromide is formed and some gas seems to be evolved. When thrown upon chlorine water the carbide is rapidly decomposed, but without ignition of the gas; the same is found to be true of bromine water. Sulphuric, nitric, and acetic acids decompose the carbide with the evolution of an inflammable gas, while sulphuric acid and potassium bichromate oxidize the compound. Alkalies also cause decomposition, probably with the evolution of acetylene.

H. P. Talbot.

On the Reaction between Zinc Sulphate and Potassium Hydroxide. By C. E. Linebarger. *J. Am. Chem. Soc.*, **17**, 358–360. — The author finds that the usual equations employed to represent the precipitation and re-solution of the zinc hydrate by potassium hydrate fail to express the true conditions. By employing a constant quantity of zinc sulphate at constant volume and temperature, but varying quantities of potassium hydroxide, he finds that for each molecule of zinc sulphate 1.62 molecules of potassium hydrate are required for the complete precipitation of the zinc, and 13.2 molecules to cause precipitation and re-solution.

H. P. Talbot.

A Study of the Chemical Behavior of Tungsten and Molybdenum and Their Trioxides. By Charles H. Ehrenfeld. *J. Am. Chem. Soc.*, **17**, 381–397. — The action of phosphorus pentachloride upon tungsten trioxide when heated out of contact with the air results in the formation of tungsten hexachloride and phosphorus oxychloride, while some tungsten pentachloride results from the decomposition of the higher compound. Molybdenum yields pentachloride mixed with some lower chlorides. Silicon tetrachloride and nitric oxide fail to attack either of the trioxides. Tungsten is converted into trioxide upon ignition in an atmosphere of nitric or nitrous oxide or sulphur dioxide, molybdenum changing to dioxide. Nitrogen peroxide converts both the metals into trioxides, while the metals remain unchanged in an atmosphere of methylamine. Tungsten trioxide when heated in a current of ethylene is reduced to a deep blue oxide, and into a blue and a brown oxide by acetylene. Molybdenum trioxide is reduced to Mo_2O_5 by ethylene, and also by acetylene, with the simultaneous formation of a molybdenum carbide, the exact composition of which was not definitely determined. Methane reduces the tungsten trioxide to W_2O_5, and the molybdenum trioxide to the

dioxide and to the metal. Ethane failed to attack either oxide; phosphine and arsine reduce the tungsten to the oxide W_3O_8 and the molybdenum to Mo_2O_5, while ammonia forms complicated compounds. When heated together with magnesium in air the tungsten trioxide is reduced to WO_2, molybdenum to Mo_2O_8; and in hydrogen the oxide of tungsten formed is W_2O_3, while the results were not definite in the case of the molybdenum. Zinc in air reduces the oxides to W_2O_5 and Mo_2O_5, and in hydrogen WO_2 and a mixture of MoO_2 and Mo_2O_5. The composition of the oxides resulting from the action of aluminum is doubtful. Very small quantities (0.004 gram) of molybdenum are dissolved by ferric chloride, with the formation of the hexachlorides of this metal; larger quantities dissolve very slowly, and even very small quantities of tungsten require long periods for solution, if complete solution is ever attained.

H. P. Talbot.

Zirconium Sulphite. By F. P. Venable and Charles Baskerville. *J. Am. Chem. Soc.*, **17**, 448–453. — It is found that when a nearly neutral solution of zirconium chloride is mixed with an excess of sulphurous acid, diluted, and boiled for some time, a heavy white precipitate is produced. When dried it is white and hard and shows a ratio of zirconium to sulphur dioxide of 2 : 1, approximately. If zirconium hydroxide be allowed to stand for two months or more covered by a solution of sulphurous acid, with frequent agitation, the solid separates into the gelatinous hydroxide and a white, finely divided substance. The latter, after drying at 95°, shows a ratio of zirconium to sulphur dioxide of 2.2 : 1. In attempting to filter the sulphite a watery layer is found to form, which on standing solidifies to a jelly. After drying between filter paper the ratio for this substance was found to be 3 : 1, and after bringing to a constant weight on a water bath it was 4 : 1. None of these correspond to the ratio for the neutral sulphite, which is 1 : 1.4, and none of the compounds appear to be of definite character. The supernatant sulphurous acid, if allowed to evaporate over sulphuric acid, yields hard crystals, the analysis of which agrees with that of hydrated zirconium sulphite, $Zr(SO_3)_2 7H_2O$. With neutral sodium sulphite the precipitate is mainly hydroxide, and with sodium thiosulphate, basic salts.

H. P. Talbot.

Argon: a New Constituent of the Atmosphere. By Lord Rayleigh and William Ramsay. *Am. Chem. J.*, **17**, 225–251; *Am. J. Sci.*, **49**, 275–297. **On the Spectra of Argon.** By William Crookes. *Am. Chem. J.*, **17**, 251–262. **The Liquefaction and Solidification of Argon.** By K. Olszewski. *Am. Chem. J.*, **17**, 262–267. — These foreign papers have been so extensively published that it is not regarded as necessary that abstracts should be made of them.

H. P. Talbot.

On the Chloronitrides of Phosphorus. By H. N. Stokes. *Am. Chem. J.*, **17**, 275–290. — A satisfactory abstract of this extended paper can hardly be made in the space at command, and reference must be made to the original for the outline of previous investigations along the same line, and the details of experimental work. The author has stated the results of his study of the properties of triphosphonitrilic chloride and of its behavior toward zinc ethyl, water, ether, and a mixture of the two latter. He has also isolated

triphosphonitrilic-tetrachlorhydrine, $P_3N_3Cl_4O_2H_2$, triphosphonitrilic chloramide, $P_3N_3Cl_4(NH_2)_2$, tetraphosphonitrilic chloride, $P_4N_4Cl_8$, and makes interesting statements regarding the behavior of these bodies. Tetrametaphosphimic acid and an oily phosphonitrilic acid will be treated of in a later paper.

H. P. TALBOT.

On the Cupriammonium Double Salts. BY T. W. RICHARDS AND GEORGE OENSLAGER. *Am. Chem. J.*, **17**, 297–305. — This paper is the third of the series (see this *Quart.*, **8**, 96). In this article four new compounds are described, with the methods of preparation. They are the following: Ammoncupriammonium acetoiodide, $Cu(NH_3)_3IC_2H_3O_2$, made from cupric acetate, acetic acid, and ammonium iodide; deep blue crystalline, monoclinic plates, unstable in air, decomposed by water and acids. Octo-cupriammonium monoiodide acetate, $7Cu(NH_3)_2(C_2H_3O_2)_2 + Cu(NH_3)_2IC_2H_3O_2$; large blue crystals, which separated on concentrating the mother liquor from the former crystals. Tetra-ammon-tricupriammonium iodide, $Cu_3I_6(NH_3)_{10}$, made from cupric acetate, acetic acid, ammonium iodide, and alcohol; crystals with a bronze lustre, unstable in the air, and decomposed by water, similar to corresponding bromine compound described in the first paper of the series. Ammonic dicupric acetate, $NH_4Cu_2(C_2H_3O_2)_5H_2O$, from cupric acetate, acetic acid, and ammonia, in the presence of alcohol; bluish green crystals, permanent in the air and soluble in water without decomposition. Cupriammonium acetate, anhydrous, $Cu(NH_3)_2C_2H_3O_2$, and hydrated, $Cu(NH_3)_2(C_2H_3O_2)_2\frac{1}{2}H_2O$, were both prepared, confirming the work of Foerster (*Ber.*, **25**, 3416).

H. P. TALBOT.

Chromates of the Rare Earths. BY CHASE PALMER. *Am. Chem. J.*, **17**, 374–379. — Earlier references are to be found relating to only two chromates of the rare earths, thorium chromate (Chydenius, *Ann. der Phys.* (*Pogg.*), **119**, 43) and cerium chromate (Pattison and Clarke, *Chem. News*, **16**, 259). Thorium chromates are treated of in the present paper, with a brief reference to chromates of zirconium. On the addition of freshly precipitated thorium hydroxide to a solution of chromic anhydride a fine orange precipitate falls, the action being more rapid at 90° than in the cold. The results of analysis correspond to the formula $Th(CrO_4)_2.H_2O$. When the solution of thorium hydroxide in the chromic acid was allowed to evaporate over sulphuric acid orange scales formed, with a composition $Th(CrO_4)_2.3H_2O$. On the addition of two molecules of potassium dichromate to one molecule of thorium nitrate, both solutions boiling, hydrated thorium chromate was thrown down. No precipitate formed at first in the cold, but after twenty-four hours the same compound was precipitated as above, but in lesser quantity; a further precipitation occurred on heating the filtrate. Potassium chromate, in the proportion of three molecules to one of the thorium nitrate, first induces a yellow precipitate of the composition $Th(OH)_2CrO_4$, while the solution becomes red, indicating the formation of potassium dichromate. If this basic chromate remains in contact with the solution it gradually changes to the orange compound already mentioned, while the solution again becomes yellow, indicating the formation of the normal chromate. One part of the hydrated salt is soluble in 284 parts of water at 22°; at a dull red heat it is decomposed into thorium dioxide and chromic oxide. It contains one molecule of water,

which is firmly bound. Whether this corresponds to the symbol $Th(CrO_4)_2.H_2O$ or to the symbol $Th\begin{matrix}Cr_2O_7\\(OH)_2\end{matrix}$, the author is unable to state. He proposes to continue the study of the chromates of zirconium and other members of the same group.

H. P. TALBOT.

On the Double Halides of Cæsium, Rubidium, Sodium, and Lithium with Thallium. BY J. H. PRATT. *Am. J. Sci.*, **49**, 397–404. — The double salts were prepared by mixing solutions of thallic halide with the alkali halide in varying proportions, evaporating, and cooling to crystallization. With bromides and iodides the conditions were improved by the presence of a little bromine or iodine. The crystals were dried between filter papers, and some of them in air, before analysis. The following compounds were prepared and their properties described, the ratios being that between the alkali metal and the thallium: (3 : 1), $Cs_3TlCl_6.H_2O$, $Rb_3TlCl_6.H_2O$., $Rb_3TlBr_6.H_2O$, $Na_3TlCl_6.12H_2O$, $Li_3TlCl_6.8H_2O$.; (2 : 1), Cs_2TlCl_5, $Cs_2TlCl_5.H_2O$, $Rb_2TlCl_5.H_2O$; (3 : 2), $Cs_3Tl_2Cl_9$, $Cs_3Tl_2Br_9$; (1 : 1), $CsTlBr_4$, $CsTlI_4$, $RbTlBr_4.H_2O$, $RbTlI_4.2H_2O$.

H. P. TALBOT.

ORGANIC CHEMISTRY.

A. A. NOYES, ABSTRACTER.

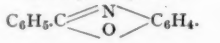
On the Saponification of the Ethers of the Sulphonic Acids by Alcohols. BY J. H. KASTLE AND PAUL MURRILL. *Am. Chem. J.*, **17**, 290–297. — The article presents a series of quantitative experiments on this reaction, which is typically expressed by the equation $C_6H_5SO_2OC_2H_5 + C_2H_5OH = C_6H_5SO_2OH + (C_2H_5)_2O$. The effect of the nature of the alcohol, of the excess of it used, of the constitution of the sulphonic acid, and of the temperature, on the saponification were all investigated. Methyl alcohol saponifies much more readily than ethyl, but the propyl alcohols do not differ from the latter appreciably in their effect. The greatest amount of saponification occurred when the proportion of alcohol to ether was 50 or 100 to 1, a larger excess of alcohol apparently causing the reaction to take place in the reverse direction. The saponification takes place at the ordinary temperature very slowly, amounting only to 13 per cent. in twenty-two days in the case of ethyl benzenesulphonate and a fifty-fold excess of methyl alcohol. Under the same circumstances the saponification of the ethyl ethers of chloro, bromo, and iodobenzenesulphonic acids equals about 30 per cent., thus showing that the presence of halogen atoms in the acid greatly facilitates the decomposition. The saponification at 100° is very rapid, reaching 85 per cent. within an hour in the case of ethyl benzenesulphonate and the fifty-fold excess of methyl alcohol and 68 per cent. with ethyl alcohol under the same conditions.

On the Two Isomeric Chlorides of Orthosulphobenzoic Acid. BY IRA REMSEN. **I. The Action of Aniline and of the Toluidines on Orthosulphobenzoic Acid and its Chloride.** BY IRA REMSEN AND C. E. COATES, JR. **II. Further Study of the Action of Aniline on the Chlorides of Orthosulphobenzoic Acid.** BY IRA REMSEN AND E. P. KOHLER. **III. Separation of the Two Chlorides of Orthosulphobenzoic Acid.** BY IRA REMSEN AND A. P. SAUNDERS. *Am. Chem. J.*, **17**, 309–368. — The crude product of the action of phosphorus pentachloride on salts of *o*-sulpho-

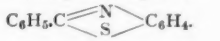
benzoic acid may be separated into two isomeric chlorides, melting at 76° and at 22°, respectively, by evaporation of the petroleum-ether solution at 0°, and mechanical selection of the crystals. The "solid" chloride (m. pt. 76°) is more conveniently obtained pure by shaking the chloroform solution for about one minute with concentrated aqueous ammonia and evaporating off the chloroform. The chloride melting at 22° is designated as the "liquid" chloride (III). Corresponding to the existence of these two isomers there are formed by the addition of the crude *o*-sulphobenzoyl chloride to an aqueous emulsion of aniline in excess two isomeric anilides, one soluble in ether and melting at 196°, the other insoluble in ether and infusible. Both are weak acids insoluble in water, soluble in alkalies and carbonates. Two isomeric toluides are also obtained both from meta and para toluidine in the same way (I). As the *fusible* anilide is alone produced by the action of the pure *solid* chloride on aniline in the presence of water, it follows that these two bodies have a corresponding constitution; and, as *o*-sulphobenzanil, $C_6H_4\begin{matrix}CO\\SO_2\end{matrix}>NC_6H_5$, is the only product of the reaction between dry aniline and the solid chloride, it follows further that the constitution is probably the symmetrical one: $C_6H_4(COCl)(SO_2Cl)$ and $C_6H_4(CONHC_6H_5)(SO_2NHC_6H_5)$. On the other hand, the infusible anilide is the principal product of the action of the liquid chloride both on dry aniline and on its aqueous emulsion, and the authors assign to these compounds the unsymmetrical structure (*e. g.*, $C_6H_4\begin{matrix}CCl_2\\SO_2\end{matrix}>O$) (II). The structure of the chlorides is further confirmed by their reactions in ether solution with dry ammonia, whereby the solid one is converted into benzoic sulphinide (saccharine), and the liquid one mainly into cyanbenzenesulphonic acid. The two chlorides are decomposed with the same readiness by boiling water. The solid one warmed with phenol gives, together with another product not identified, diphenyl *o*-sulphobenzoic ether, a body melting at 118°, readily soluble in hot alcohol and sparingly in cold. By the action of benzene and aluminum chloride on the mixed chlorides or on the solid chloride, *o*-benzoylbenzenesulphonyl chloride, $C_6H_5COC_6H_4SO_2Cl$, is at first produced, and by continued action, *o*-benzoyldiphenylsulphone, $C_6H_5COC_6H_4SO_2C_6H_5$, results. The first of these substances crystallized from ether melts at 96°–97°, and reacts with caustic potash to form potassium *o*-benzoylbenzenesulphonate, $C_{13}H_9SO_4K + H_2O$ (which on fusion with dry potash is almost quantitatively decomposed into potassium benzoate and benzenesulphonate), with alcohol to form an ethyl ether melting at 126° and readily saponified by hot alcohol, with ammonia to form a lactim (m. pt. 163°), and with aniline to form an anilide (m. pt. 143°–145°). The *o*-benzoyldiphenylsulphone (m. pt. 184°) is decomposed by fusion with potash into potassium benzoate and diphenylsulphone (III). Incidentally a number of other new compounds are prepared and described, namely, the acid and neutral *o*-sulphobenzoates of aniline and the three toluidines; the above mentioned *o*-sulphobenzanil (m. pt. 190.5°) and the corresponding tolils prepared in the same way from the toluidines; and the anilic and paratolilic acids produced by the action of boiling caustic soda on the anil and paratolil (I). Orthosulphobenzanil is studied quite fully in order to establish its symmetrical constitution. It is obtained by the oxidation of *o*-toluenesulphonanilide with potassium permanganate and heating of the oxidation-product, as well as by the method before mentioned. The anil when boiled with dilute hydrochloric acid is transformed into the acid aniline salt of *o*-sulphobenzoic acid; when boiled with aniline, into the fusible anilide of that acid (II).

On the Action of Benzimidomethyl Ether on Aromatic Ortho Compounds. By H. L. Wheeler. *Am. Chem. J.*, **17**, 397–403. — Benzimidomethyl ether (prepared by digesting silver benzamide suspended in ether with an excess of methyl iodide, or by the action of gaseous hydrochloric acid on a mixture of benzonitrile and methyl alcohol) is an oil not solidifying at —30°, soluble in acids, insoluble in alkalies. In contact with water it slowly decomposes into benzamide and methyl alcohol. Heated to 100°–110° with *o*-amidophenol, *o*-amidothiophenol, *o*-phenylenediamine, and *o*-toluylenediamine it yields, respectively, the following known anhydro bases:

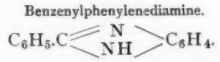
Benzenylamidophenol.



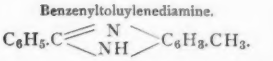
Benzenylamidothiophenol.



Benzenylphenylenediamine.



Benzenyltoluylenediamine.



On the Action of Some Inorganic Cyanides upon Chlorocaffeine. By M. Gomberg. *Am. Chem. J.*, **17**, 403–420. — Chloro- and bromocaffeine ($C_8H_9N_4O_2Br$) when boiled with potassium cyanide dissolved in 80 per cent. alcohol do not yield the cyanide, but some hydroxycaffeine and the carboxylamide ($C_8H_9N_4O_2CONH_2$), an amorphous infusible body, insoluble in water, dilute acids, and organic solvents, soluble in strong acids. The author describes a variety of unsuccessful attempts to prepare the cyanide directly, in which other solvents for the potassium cyanide and other metallic cyanides were used. In some cases some cyanide was formed, but the transformation was never complete, and the product could not be freed from unchanged chlorocaffeine. Cyanocaffeine was, however, obtained by heating the carboxylamide to 200° with phosphorus pentoxide for several hours. It is a white crystalline substance melting at 151°, subliming at 160°, soluble in hot water, hot alcohol, methyl alcohol, and chloroform, insoluble in ether. It is not readily hydrated except in the presence of potassium cyanide. — The carboxylamide is converted at 100° by dilute sulphuric acid (1 : 1) into caffeine, carbon dioxide, and ammonia. At a lower temperature some caffeinecarboxylic acid is formed, but the best method of preparing the latter is to pass nitrogen trioxide into the cold sulphuric acid solution until on dilution with water an amorphous precipitate is no longer produced. The acid crystallizes in silky needles melting at 225°; it is insoluble in cold water and alcohol, soluble in these solvents when hot, insoluble in chloroform (unlike most caffeine compounds), carbon bisulphide, and benzene. It splits off carbonic oxide very readily when heated dry or with dilute acids. Its sodium, potassium, calcium, barium, copper, and silver salts, and its methyl and ethyl ethers (prepared from the silver salt and the alkyl iodides), are described.

Camphoric Acid. By W. A. Noyes. *Am. Chem. J.*, **17**, 421–434. — This is a third paper by the author (see *Am. Chem. J.*, **16**, 505) contributing to the knowledge of the constitution of camphoric acid and camphor. It is here shown that dihydroaminocampholytic acid, $C_8H_{14}(NH_2)(CO_2H)$ (which is derived directly from camphoric amide, $C_8H_{14}(CONH_2)(CO_2H)$), is decomposed by nitrous acid into a *tertiary beta* hydroxy acid, $C_8H_{14}(OH)(CO_2H)$, and into campholytic acid, $C_8H_{13}(CO_2H)$. The hydroxyl group is tertiary, since the acid is very stable towards potassium permanganate and chromic acid mixture. It is probably β to the carboxyl group, since of the remaining positions the γ is excluded by the fact that the acid forms no lactone, the

δ by the existence of camphoric anhydride, and the α by the differences in the reactions of the two amino acids. It therefore follows, as Walker assumed, that camphoric acid contains the group $-CH(CO_2H)-CR(CO_2H)-$. This is further confirmed by the behavior of campholytic acid towards dilute sulphuric acid as an $\alpha\beta$ unsaturated acid, since it does not form a lactone as $\beta\gamma$ acids do. — Dihydro-hydroxycampholytic acid, prepared as above stated, melts at 132°, and is moderately soluble in water and ether, very difficultly in ligroin, and easily in alcohol. Treated with fuming hydrobromic acid a hydrobromide, $C_8H_{14}BrCO_2H$ (m. pt. 98°–100°), is formed identical with the addition-product of cis-trans-campholytic acid. The hydroxy acid and cis-trans-campholytic acid on standing with dilute sulphuric acid (1 : 1) are quantitatively transformed into cis-campholytic acid, which is identical with the camphothetic acid of Walker (*J. Chem. Soc.*, **63**, 504) and the isolauronolic acid of Koenigs and Hoerlin (*Ber.*, **26**, 814). The acid crystallizes in rectangular plates, melting at 133.5°, very difficultly soluble in cold water, but easily in alcohol and ether. Its bromine and hydrobromic acid addition-products are described. — The products of the action of nitrous acid on aminolauronic acid, $C_8H_{14}(NH_2)(CO_2H)$, consisting of a hydrocarbon, a lactone, and an unsaturated acid, have now been more carefully studied. The hydrocarbon has the composition C_8H_{14}, boils at 122°, and has a specific gravity at $\frac{20°}{4°}$ of 0.8004. The lactone (called iso-campholactone) melts at 23°, and is isomeric, not identical with the campholactone of Fittig and Worringer (*Ann. Chem.*, **227**, 10). The acid, γ-lauronolic acid, identical with the allo-campholytic acid of Walker and Henderson (*J. Chem. Soc.*, **67**, 341), is a $\beta\gamma$ acid of the composition $C_8H_{13}CO_2H$. Heated with dilute sulphuric acid to 100° it is changed to campholactone (m. pt. 48°–49°).

On Some Experiments with Acetylacetone and Acetacetic Ether. By Richard S. Curtis. *Am. Chem. J.*, 17, 435–443. — The two products obtained by Nef (*Ann. Chem.*, 277, 73) by the digestion of silver acetylacetone with an excess of ethyl iodide are shown to be isomeric substances, the one soluble in caustic alkalies being presumably α-ethylacetylacetone, the insoluble one, α-acetyl-β-ethoxypropylene. — The author also shows that, contrary to the assumption of Claisen, acetacetic ether, like the oxymethylene compounds and the fatty acids, is etherified by means of absolute alcohol and hydrochloric acid, a 15 per cent. yield of β-ethoxycrotonic ether being so obtained. — By the addition of bromine to β-ethoxycrotonic ether in ether solution at —10° a variety of not fully identified products are produced. The dibromide is not stable at that temperature. — The copper salts of α and γ-bromacetacetic ethers were investigated in the hope of finding therein a means of separating the two ethers, but with only partial success. The author believes, however, to have proved with their help that the product of the action of bromine on acetacetic ether is a mixture of the α- and γ-bromacetacetic ethers.

On Some Azo and Azimido Compounds. By W. G. Mixter. *Am. Chem. J.*, 17, 449–453. — Benzoylazotoluide: $[C_6H_3.CH_3(1).NHC_7H_5O(4).N(5)]_2$, acetylazotoluide: $[C_6H_3.CH_3(1).NHC_2H_3O(2).N(5)]_2$, and benzoylazoxylide: $[C_6H_2.CH_3(1).CH_3(3).NHC_7H_5O(4).N(5)]_2$ are prepared by the reduction of the corresponding nitro compounds in alcoholic solution with zinc and ammonia. These azo compounds are almost insoluble in alcohol, but

crystallize from boiling acetic acid. — Benzoylazimidotoluene: $C_6H_3.CH_3(1).N_2(4).NC_7H_5O(5)$ (m. pt. 125°) and benzoylazimidoxylene: $C_6H_2.CH_3(1).CH_3(3).NC_7H_5O(4).N_2(5)$ (m. pt. 111°) are obtained by the addition of potassium nitrite to an acid solution of benzoyldiamidotoluene and benzoyldiamidoxylene, respectively. Both are easily soluble in alcohol. Azimidoxylene, resulting from the treatment of the second compound with hot, strong hydrochloric acid, is a white powder slightly soluble in cold water, but readily soluble in acids, ammonia, alcohol, and ether.

On the Action of Certain Alcohols with Metadiazobenzenesulphonic Acid. By W. B. Shober and H. E. Kiefer. *Am. Chem. J.*, 17, 454–461. — This acid, when boiled at various pressures (from 400 to 800 mm.) with methyl, ethyl, or propyl alcohol, undergoes two distinct reactions, the diazo group being replaced partly by hydrogen and partly by the methoxyl, ethoxyl, or propoxyl group. Increase of pressure (or more correctly the increase of temperature produced by it, which unfortunately the authors do not state) causes, in the case of methyl and ethyl alcohols, at least, the second of these reactions to take place to a relatively greater extent. The previously investigated *para*-diazobenzenesulphonic acid (Shober, *Am. Chem. J.*, 15, 379) behaved quite differently, as the hydrogen replacement took place exclusively, except in the case of *methyl* alcohol, at ordinary and increased pressure. It moreover requires hours for its decomposition where the meta acid requires minutes. — The reaction-products were separated by conversion to the amides and mechanical selection of the crystals. Meta methoxy, ethoxy, and propoxy-benzenesulphonamides melt at 128°, 126°, and 122°, respectively.

On Some Experiments in the Anthracene Series. By C. E. Linebarger. *J. Am. Chem. Soc.*, 17, 354–358. — The author describes several unsuccessful attempts to prepare the compound $C_6H_4\begin{smallmatrix}C\\ \|\\ C\end{smallmatrix}C_6H_4$. Monobromanthracene heated alone to 300°, or with alcoholic potash in closed tubes, or with solid potash, gave only anthracene. Anthracene also resulted from the action of sodium in xylene solution on dibromanthracene.

On the Crystal Form of Borneol and Isoborneol. By William H. Hobbs. *Am. J. Sci.*, 49, 449–452. — Crystallographic measurements show that the alcohol, $C_{10}H_{18}O$, obtained from the oil of black spruce and from that of fir balsam is borneol, while that obtained from the oil of turpentine in benzene is identical with isoborneol (*J. prakt. Chem.*, 49, 1), except in the one respect that it is optically negative. New crystallographic data in regard to these two substances are communicated.

Vegetable Chemistry.

A. A. Noyes, Abstracter.

Basswood-oil. By F. G. Wiechmann. *Am. Chem. J.*, 17, 305–308. — From a sample of sound basswood ether was found to extract 5.24 per cent. of a saponifiable oil having the following characteristics: Specific gravity, $\frac{15°}{15°}$, 0.938; congealing point, —10°; saponification-equivalent, 315; iodine absorption, 111; color, olive brown; Heydenreich's reaction, yellow and red brown. It thus resembles cottonseed oil in its properties. In a second sample of basswood, which had lain under water for a long time, the oil was found to

have undergone decomposition, so that on saponification and distillation with steam it yielded a considerable proportion of volatile fatty acids of mean combining weight, 92.

The Sugar of the Agave Americana. By W. E. Stone and D. Lotz. *Am. Chem. J.*, 17, 368–371. — The authors have examined two distinct samples of this sugar, and find it to be identical in all its properties with sucrose, contrary to the results of Michand and Tristan (*Am. Chem. J.*, 14, 548), who stated that their sugar was optically inactive.

The Furfurol-yielding Constituents of Plants. By C. F. Cross, E. J. Bevan, and C. Beadle. *J. Am. Chem. Soc.*, 17, 286–289. —The purpose of the article is to point out that de Chalmot in a recent paper (*Am. Chem. J.*, 16, 589) substantially accepts the opinions of the authors that the furfurol-yielding constituents of plants are not necessarily pentoses or pentosans, but in many cases oxidation derivatives of cellulose still containing six carbon atoms.

Apparatus.

A. H. Gill, Abstracter.

A Cheap Form of Self-Regulating Gas Generator. By W. W. Andrews. *J. Am. Chem. Soc.*, 17, 304–306. — Reference must be made to the original article for the description. The apparatus would seem to merit special attention on account of its cheapness, convenience, and safety. The quality of gas is more even than that furnished by the Kipp generator.

A New Hydrogen Sulphide Generator. By J. I. D. Hinds. *J. Am. Chem. Soc.*, 17, 420. — The apparatus is very similar to that of Koninck.

Absorbent Blocks. By P. T. Austen and W. H. Broadhurst. *J. Am. Chem. Soc.*, 17, 472–473. — To replace the unglazed plates which are used for drying substances in the laboratory the authors propose a thorough mixture of equal parts of infusorial earth and plaster of Paris, which is so moistened as to work easily. A mould is prepared, consisting of a sheet of slightly oiled glass with strips of glass serving as divisions, upon which the mixture is poured and allowed to harden, after which the blocks are detached and dried at 110°–120° C.

Some New Laboratory Apparatus. By E. Sauer. *J. Am. Chem. Soc.*, 17, 474–476. — The article pictures and describes a shaking apparatus, consisting of a miniature freight car on a track, having a capacity for bottles up to six liter, two Witt's stirrers, and a pulley for a centrifugal machine, all driven by a Henrici hot-air engine. — Lupp's illuminating apparatus is also described. It consists of a tripod mounting a concave mirror, over which is placed the beaker containing the fine precipitate, or any color, the depth of which is to be estimated. It would seem to be especially useful in titrating in cloudy weather, since any change would be readily recognized in the strongly illuminated liquid.

An Arrangement for Washing Precipitates with Boiling Water. By F. F. Jewett. *J. Am. Chem. Soc.*, 17, 517–518. — A description and sketch of an apparatus for the mentioned purpose.

An Automatic Mercury Vacuum Pump. By M. I. Pupin. *Am. J. Sci.*, 49, 19–21. — For a description of the apparatus reference must be made to the original article.

Technical Chemistry.

The Contributions of Chemistry to the Methods of Preventing and Extinguishing Conflagration. By T. H. Norton. *J. Am. Chem. Soc.*, 17, 137–147, 251–260, 361–380. — The author begins by stating the annual fire losses, which are, in round numbers, $200,000,000, of which sum America contributes more than $90,000,000, amounting to one fifth the annual profits of all the industries of the country, and to this must be added the cost of water supply and fire departments, amounting to one third more. From 80 to 90 per cent. of this loss might be easily avoided by the adoption of slow-burning construction and the use of fireproof material. — The various fire extinguishers and hand grenades are first discussed; these include the chemical engines, liberating carbon dioxide, and the various extinguishing powders, which by their combustion yield inert gases, as sulphur and carbon dioxides. These are usually composed of about sixty parts saltpeter, thirty-five parts sulphur, and five of charcoal. The hand grenades contain about 25 per cent. solutions of the chlorides of magnesium, calcium, ammonium, and sodium, mixed in various proportions, and costing about 1 per cent. of their selling price. In this division of the subject there seems to be little chance for further contributions of any real value; a non-inflammable, non-corrosive, and non-freezing liquid for filling the pipes of automatic sprinklers would, however, fill a long-felt want. — The second part of the paper treats of the methods of fireproofing fabrics and wood. These consist in depositing upon these substances either some insoluble compound or some salt, which, upon heating, liberates fire-extinguishing gases. Of the forty-four salts experimented with by Versmann and Oppenheim in 1859 but two, ammonium phosphate ($(NH_4)_2HPO_4$) and sulphate, gave good results. The others were objectionable on account of hardening the fabric, keeping it damp, affecting its strength, or their high cost. Sodium tungstate solution (1.14 sp. gr.), containing 3 per cent. of sodium phosphate, is especially to be recommended for light fabrics which are to be ironed. The composition of quite a number of the later mixtures is given. Apparently the first compound used for wood was silicate of soda applied as a paint, which changed its composition afterwards and afforded no protection. The pores of the wood were then filled with calcium sulphate, by double decomposition, by exhausting the air and allowing solutions of calcium sulphide and copperas to enter alternately. Wood so prepared is largely used in England in public works. Kyanizing, burnettizing, boucherizing, all render wood less inflammable. In place of impregnation as a means of preventing fire, recourse was next had to covering the outside of the wood with a protective coating. Various siliceous paints — water glass, with additions of quartz, alumina, zinc oxide, iron oxide, or powdered glass — have been used; a still later addition is a mixture of ground asbestos, potassium aluminate, oil driers and gummy matters, and this makes the best type of a protective coating. The methods of testing the efficiency of the various agents are given. The first method (Lochtin's) is by impregnating strips of filter paper 50 cm. long and 5 cm. broad, and igniting it; the author uses thin strips of pine wood 8 cm. long and 1 cm. wide. Boudin and Donny use wooden rods 39 cm. long and 15 mm. square, impregnated with the sub-

stances, which are rotated over a series of five Bunsen burners, consuming 7 cubic feet of gas per hour. A still more rigorous test, and one approximating to the conditions in practice, consists in producing a flame directly in contact with the protected surface. Six rows of six rods 20 cm. by 15 mm. square, alternately crossing each other, are piled up, leaving an open space 6 cm. square in the center. Little bundles of splints, weighing 35 grams each, are introduced, ignited, and the effect noted, the charge being repeated if necessary. The results are tabulated, so that the efficiency of the various compounds may be seen at a glance. — The fireproofing compounds act in two ways, either by evolving some inert gas which extinguishes combustion or by producing some non-conducting covering which protects the outside zone of charcoal from the air. — The field for further improvement seems to lie in displacing petroleum products as lighting agents and in the more extensive use of metal as structural material. Further experiments with the borates and silicates upon fabrics and the combination of injecting the wood and painting it are suggested.

A. H. GILL.

The Manufacture of Carbide of Calcium by Electrolysis. BY F. BREDEL. *Am. Gas Light J.*, **52**, 260–261. — The author calculates that the cost of production of a ton of calcium carbide is $40.

A. H. GILL.

Studies in Carbide of Calcium. BY M. P. WOOD. *Am. Gas Light J.*, **52**, 402–404. — The literature of the various methods of preparation of acetylene is given, and also a statement of its properties.

A. H. GILL.

Carbide of Calcium. BY H. L. DOHERTY. *Am. Gas Light J.*, **52**, 407–408. — The preparation and properties of the substance are given. It is stated that it can be produced at a price of $30 to $60 per ton, yielding 10,000 cubic feet of acetylene, equivalent to 120,000 cubic feet of 20 candle power gas. The author thinks that little can be hoped for from this gas as an enricher on account of its specific gravity, but that it would be useful alone if an automatic machine were built to generate it.

A. H. GILL.

Acetylene. BY F. L. SLOCUM. *Am. Gas Light J.*, **52**, 802–803. — The properties and various methods of production are given, especially from calcium carbide, the latter being estimated to cost from $15 to $100 per ton. The author thinks that there is little hope of the gas ever becoming a competitor of coal and water gas.

A. H. GILL.

Acetylene as an Enricher. BY E. G. LOVE. *Am. Gas Light J.*, **53**, 82–84. — The candle power of the pure gas is 230 for 5 cubic feet per hour consumption. The author thinks that the chief use will be to enrich carburetted water gas, increasing the candle power from 7.6 to 20, at a cost of 15 cents per 1,000 cubic feet. The most hopeful outlook for the use of the gas is its generation and consumption by itself at a rate of 1 to 1.5 cubic feet per hour, giving about 56 candle power.

A. H. GILL.

Gas from Coke Ovens. By SCHNIEWIND. *Iron Age*, 55, 588. — A table of the analyses of the various kinds of gas is given, that from the Otto-Hoffmann coke ovens having about double the heating value of water gas, three and one half to five and one half times that of producer gas, and six times that of blast furnace gas. Seventy volumes of natural gas are theoretically equal to one hundred of coke oven gas; practically, however, eighty volumes of natural gas are necessary, because double the theoretical amount of air is required to burn it. On account of the difference in specific gravity the same pipe lines will furnish a proportionately increased quantity of oven gas, so that no change in the piping would be required to transmit it. Sixty Otto-Hoffmann ovens, coking 420 tons coal daily, furnish 9,100 cubic feet of gas per ton, or 3,822,000 cubic feet, of which one half is used to coke the coal, and the remainder, equal to 61 tons of coal, or 1,450 horse power, is available for use. To supply the needs of Pennsylvania it would require sixty-one plants of this capacity. — The paper further states that whether coal be coked or distilled for gas the amount of heat required is practically the same. One cubic meter of the gas yields 5,195 calorie or 265 British thermal units per cubic foot. The waste heat from the ovens can be used for making steam. Results of German practice are also given.

A. H. GILL.

The Heating Power of Wyoming Coal and Oil, with a Description of the Bomb Calorimeter. By E. E. SLOSSON AND L. C. COLBURN. *Bull. University Wyoming.* (Abstract, with complete tables, *J. Soc. Chem. Industry*, 14, 353). — The authors have determined the water, volatile combustible matter, fixed carbon, ash sulphur, and the heating value (by the Mahler Bomb) of fifty-four samples of coal and eight of oil. The petroleums have nearly double the heating value of the coals. — The authors consider the boiler test of fuels, where all factors can be accurately determined, of great value, but that the calculation from the analyses, which in themselves are tedious and delicate to perform, has many disadvantages, and recommend a calorimeter test as the most satisfactory. The Thomson calorimeter was discarded on account of the impossibility of making accurate corrections for the various losses of heat, as from the combustion gases, the imperfect combustion of the carbon, and the solution of the salts. These corrections were stated by the manufacturers of the instrument to be 10 per cent., and were found to be more nearly 30 per cent. The Berthelot calorimeter is too expensive, costing $1,500; the Mahler, costing but $150, yields practically identical results. The Regnault-Pfaundler formula (*Ostwald's Lehrbuch d. allgemeinen Chemie*, 1, 572) gave better results for the cooling correction than that of Mahler.

A. H. GILL.

Method of Determining Flashing and Burning Points of Combustible Liquids. By C. B. DUDLEY AND F. N. PEASE. *Am. Eng. R. R. J.*, 49, 201–202. — The apparatus is very simple, consisting of a $2\frac{3}{4}''$ Berlin porcelain dish, which serves as the cup, supported in a sand bath, heated by a Bunsen burner. The apparatus is supported upon a tripod carrying a rod, from which the thermometer is suspended; the porcelain tube used with Rose's crucible makes the best possible jet for a testing flame, which latter should be $\frac{1}{4}''$ long and $\frac{1}{8}''$ in diameter.

The dish is filled with the liquid to be tested within $\frac{1}{4}''$ of the top and the thermometer hung in the center of the dish so that it does not touch it; it is then slowly heated and the test flame passed slowly *across* the dish $\frac{1}{2}''$ above the liquid and just in front of the thermometer. This is continued until the vapor of the liquid ignites with a slight flash, when the temperature, which is the flashing point, is noted. These directions must be carefully observed. — The condition which most influences the determination of the flashing point is the rapidity of heating; the greater this is, the more the flash and burning points are lowered. Another condition is the frequency with which the test flame is applied. In the Pennsylvania Railroad laboratory the practice is to raise the temperature 12° F. per minute in the case of 150° fire-test petroleum and of "wood preservative," and 15° per minute in the case of 300° and 500° fire-test petroleums and of paraffine and well oils; and in accordance with the State law the flame is applied for each succeeding 7° rise. Duplicate determinations vary from 1° to 7° F.

A. H. GILL.

Method of Taking Cold Test and Chilling Point of Oils and Other Liquids. BY C. B. DUDLEY AND F. N. PEASE. *Am. Eng. R. R. J.*, 49, 332–333. — Detailed directions are given for taking the cold test by cooling down 1 ounce of the oil in a 4-ounce bottle placed in a freezing mixture and noting the thawing temperature of the mass. The chilling point, or lowest temperature at which the liquid remains clear, is similarly taken. Directions for making the various freezing mixtures are also given.

A. H. GILL.

Accuracy of the Dyeing Test. BY CHARLES S. BOYER. *J. Am. Chem. Soc.*, 17, 468. —The author has made comparative dyeing tests of two samples of chipped logwood and compared the results with those obtained by analyses of the same samples by Schreiner's hide-powder method (*Chem. Ztg.*, 1890, 961) and also by Trimble's volumetric color method. He also compared results obtained in the examination of extracts of sumac by dyeing tests and by hide-powder method. The author's conclusions are that a dyeing test when applied to chipped logwood and to unadulterated extracts of logwood and of sumac yield results which compare favorably with the best methods of analytical chemistry; also that the results of the dyeing test have a practical value.

J. W. SMITH.

Chemical Brick for Glover Towers. BY IRVING A. BACHMAN. *J. Am. Chem. Soc.*, 17, 360–361. — A short article containing the tabulated results of tests of brick made from Aiken, S. C., clays. The results will be of interest to sulphuric acid makers, as the tests show the brick to be of excellent quality.

F. H. THORP.

On the Manufacture of Soluble Nitrocellulose for Nitrogelatine and Plastic Dynamites. BY J. E. BOMEN. *J. Am. Chem. Soc.*, 17, 411–419. — In this paper are presented important facts bearing on the preparation of a nitrocellulose which is soluble in nitroglycerol. This must be a trinitrocellulose, as higher nitrated products are insoluble. To prepare it much care

and attention are necessary. Cotton waste is recommended as good material. The important factors in the process are the proportion and strength of the sulphuric and nitric acids used, the time that the cotton and acid mixtures are in contact, the temperature, etc. Too strong sulphuric acid, or an excess of it, tends to form cellulose hydrate, which, being more readily nitrated than cellulose, results in the formation of too highly nitrated derivatives. Or some of the cotton may be converted to glucose, which when nitrated forms nitrosaccharose, an insoluble and dangerous admixture. With too little sulphuric acid the nitric acid soon becomes too dilute to complete its action. The author finds a temperature of 70° C. gives the most uniform product. He uses forty parts of nitric acid (sp. gr. 1.430) and sixty parts of sulphuric acid (sp. gr. 1.835). The mixing is best done in lead-lined tanks with water jackets, and compressed air delivered through a perforated lead coil is used to stir the mixture. For nitrating, earthenware pots (depth 16 in., diameter 13 in.) set in troughs filled with water at 70° C. are recommended. Each pot holds 45 pounds of mixed acids, sufficient for 2 pounds of cotton, which is rapidly immersed by means of a fork. The time of nitrating is seventy minutes, the cotton being turned once or twice. Excess of acid is squeezed out by the use of the fork and the nitrated cotton put through a centrifugal machine. It is then plunged into cold water in a large tank and thoroughly washed with it and then with a sal soda solution. It then passes through a pulping machine and is reduced to a very fine pulp, on the fineness of which depends, to a great extent, its solubility. The pulp is thoroughly dried at 80° C. and then passed through a fine sieve. This nitrocellulose should contain from 20.5 to 21.8 per cent. of NO_3, and should dissolve in thirteen and one third parts of nitroglycerol, within twenty minutes forming a transparent jelly. The cost is from thirty-five to forty cents per pound, which may be reduced, it is suggested, by the utilization of waste acids from the nitroglycerol manufacture.

F. H. Thorp.

The Analysis of Used Liquors in Chrome Tannage. By Carlton B. Heal and H. R. Proctor. *Leather Manufacturer*, **5**, 67–70. — The authors first discuss the methods of determination of free chromic acid in the bath before and after use. The method of N. McCulloch (*Chem. News*, **55**, 2), using hydrogen peroxide and ether, and titrating with standard potassium chromate until the disappearance of the blue color, was found, after slight modification, to give good results. The authors found that the addition of excess of standard soda and titration back with standard acid gave a sharper end-point than direct titrating with potassium chromate. Excess of standard soda is first added to the bichromate solution and then previously neutralized hydrogen peroxide (1–2 cc. of a ten-volume solution for 25 cc. of half normal bichromate) and ether to a depth of an inch, and the titration with standard acid is then made in 4-ounce glass-stoppered bottles, shaking well after each addition of acid. — The method of E. Donath (*Ztschr. Anal. Chem.*, **18**, 78), which uses manganese sulphate for detecting chromate in the presence of bichromate and depends on the formation of a brownish black precipitate in the boiling solution, was found unreliable. When copper sulphate is added to the chrome liquor and it is titrated with standard soda much better results are obtained, but the brown precipitate is difficult to see in the deep-colored chrome liquor. The total chromic acid in the liquors was estimated by titration with soda, using phenolphthalein as indicator. Having tested these

methods of analysis, the authors tried the experiments as follows: To determine (1) the rate and extent to which the free chromic acid is taken up by the pelt; (2) the excess of chromic acid over the quantity necessary to produce good leather, which raw pelt will absorb when placed in successive baths of the same strength; (3) the effect of using remade liquors, and also how far the bichromate can be reduced in the chrome liquor while keeping the free chromic acid constant; (4) the extent of the action of the sulphuric acid produced from the sulphurous acid in the reducing bath on the sodium thiosulphate remaining in it. The experiments were carried out with much care and detail, and the article is worthy of the attention of all chemists interested in chrome tannage.

F. H. THORP.

A Study of Glass and the Relation of its Properties to its Chemical Composition. BY ROBERT LINTON. *Proc. Eng. Soc. Western Pennsylvania*, 11, 119–136. — The author shows that the compositions of various kinds of glass approach more or less closely a definite formula for each variety. Good samples of window and plate glass approximate the formula $Na_2O.CaO.5SiO_2$, while crystal appears to have the formula $Na_2O.2PbO.12SiO_2$. The author inclines to the theory that the alkali unites with part of the silica to form an acid silicate (as $Na_2O.4SiO_2$), which "may then act as a solvent for the other base or bases and the remaining silica, which unite and remain as silicates in solution." Devitrification is due to the separation of true crystals of glass from the solution in the silicate of the alkali. The hardness, durability, and other properties of glass are due to the quantity and nature of the silicates held in solution by the alkali silicate. In alkali-lime glass the dissolved silicate is that of calcium, and in the best grades of plate, window, and bottle glass the bases are present in nearly equal molecular proportions. The effect of too much or too little lime is also shown. Magnesia makes the glass harder, more brilliant, and more infusible. Alumina increases the fusibility and also the tendency to devitrification. Baryta, lime, borax, zinc, or magnesia may be added to lead glass to give a harder and more durable glass. Baryta is generally used, as it replaces some of the lead or lime, yielding a glass which clears up easier than soda-lime glass, and makes the lead glass more durable without materially altering its properties. After considering the subject of colored glass and the chemical problem involved in decolorizing ordinary transparent glass the author discusses opaque glass, which owes its opacity to the addition of some white amorphous substance which is held in suspension in the glass. This is generally a fluoride or phosphate, sometimes a stannate, antimonate, or oxide. Melts of opaque glass when allowed to stand some time in the furnace become clear, owing to the decomposition of the fluoride and escape of fluorine as silicon tetrafluoride. Glass often contains borates, and when present in large quantity these impart a slight bluish tint. Arsenic is often found in glass, showing that it does not entirely volatilize, as is claimed by most glass makers; but alkali-lime glass seldom contains more than a trace of arsenic. The article contains a few misprints, but, as a whole, is very readable and instructive.

F. H. THORP.

GEOLOGICAL AND MINERALOGICAL CHEMISTRY.

W. O. CROSBY, ABSTRACTER.

On Three New Analyses of Sodalite from Three New Localities. BY L. MCI. LUQUER AND G. J. VOLCKENING. *Am. J. Sci.*, 49, 465–466. — The three localities are Hastings County, Ontario; Ural Mountains, Asia; and Congo State, Africa. Following are the analyses:

	Sp. gr.	Cl.	SiO_2.	Na_2O.	Al_2O_3.	CaO.	K_2O.	Total.
Ontario	2.303	6.79	37.34	25.01	31.25	0.38	0.74	101.51
Urals	2.328	6.65	37.28	24.74	31.60	0.46	0.93	101.66
Congo.	2.363	6.46	37.85	25.43	30.87	0.51	0.22	101.34

Oxygen equivalents for chlorine should be deducted from the totals as follows: Ontario, 1.53; Urals, 1.50; Congo, 1.46.

The Age and Succession of the Igneous Rocks of the Sierra Nevada. BY W. H. TURNER. *J. Geol.*, 3, 385–414. — The author refers the igneous rocks of the Sierra Nevada to three general series: (1) Granite series; (2) magnesian series; (3) porphyrite and amphibolitic rocks. Under granite, which forms much the larger part of the range, are included the potash-poor granite or granodiorite of Becker, or tonalite of Vom Rath, and the porphyritic granite. The magnesian series comprises serpentine, talc, and tremolite schists, with some other associated amphibolitic schists, the entire series being derived from basic igneous rocks. The oldest rocks encountered in this study are the Carboniferous limestones and slates, with occasional layers of conglomerate. Among the pebbles of the conglomerate are hornblende and mica-porphyrites and an augite-syenite, a partial analysis of which gave Dr. Stokes: SiO_2, 55.45; MgO, 4.11; K_2O, 5.18; Na_2O, 1.73. A rock in place, which is the probable source of these pebbles, gave the same analyst: SiO_2, 55.04; MgO, 3.41; K_2O, 1.41; Na_2O, 4.27. The Sierra Buttes are formed of a fine-grained rock containing abundant porphyritic quartzes. The extremes of three analyses of this rock are: SiO_2, 73.62–79.41; CaO, .09–2.55; K_2O, 2.23–4.27; Na_2O, 2.46–3.78. The lime is regarded as secondary carbonate, and the rock is classed with the quartz-porphyries, in spite of its low proportion of potash. Other analyses show the essential agreement of the quartz-porphyries and quartz-porphyrites or dacites. Analyses of the following pre-Tertiary igneous rocks are tabulated on page 403: Porphyrite, augitic tuff, melaphyre (?), peridotite, diabase, quartz-mica-diorites (granodiorites), hornblende-mica-porphyrite, porphyritic granodiorite, aplites, diorite (?). These analyses are very complete, no fewer than twenty constituents having been determined. Similar analyses of the following Tertiary igneous rocks are also tabulated: Rhyolite, older basalt, Table Mountain basalt, hornblende-pyroxene-andesite, hornblende-andesite, late pyroxene-andesites, quartz-andesites, late doleritic basalt. The rocks are named in each series in the supposed order of succession. The analyses were made almost exclusively by Dr. W. F. Hillebrand, of the United States Geological Survey.

Volcanic Dust. By H. J. Harnly. *Science*, **2**, 77–78. — Describes briefly a large deposit of volcanic dust in central Kansas. It forms a bed from 2 to 4 feet in thickness, extending over an area at least fifteen miles in diameter. An analysis by Mr. James Gilbert afforded: SiO_2 and insol. residue, 92.32; Fe_2O_3 + Al_2O_3, 2.66; CaO, 0.60; MgO, 2.88; H_2O, 1.22; with traces of P, CO_2, Cl, Na, K. Under the microscope it is found to consist almost wholly of microscopic, transparent siliceous flakes of various irregular forms. The composition suggests to the abstracter a fine quartz sand (quartz flour), rather than any volcanic product, a conclusion which would diminish the difficulty of accounting for its occurrence in central Kansas.

On the Presence of Fluorine as a Test for the Fossilization of Animal Bones. By Thomas Wilson. *Am. Naturalist*, **29**, 301–317, 439–456, 719–725. — This paper, after the introductory paragraphs, is, for the most part, a translation from the French (*Annales des Mines*, 2d Bull. of 1890, 155, *et seq.*) of a complete and elaborate investigation by M. Adolphe Carnot; but the importance and interest of the subject will, perhaps, warrant a brief indication of its main points. The primary object of this investigation was to establish a criterion for determining the relative antiquity of fossil bones, and especially of human bones found in prehistoric graves, caverns, etc. The methods of analysis are first described, and then complete analyses of modern bones from twelve different sources — human, mammalian, and reptilian — are given to show their substantial agreement in composition. The proportion of calcium fluoride in all true and unaltered bones falls, in every instance, between $\frac{1}{3}$ and $\frac{1}{2}$ per cent. The proportions of phosphoric acid and of fluorine are next given for modern bones from twenty different sources, including man, mammals, reptiles, birds, and fishes. The P_2O_5 is found to vary from about 37 to 42 per cent., and the F from 0.16 to 0.31 per cent.; and the important fact is noted that the ratio of F to P_2O_5 is, on the average, only about one twentieth as great as in apatite. Numerous analyses of fossil bones from various formations are given and quoted to show the general character of the changes involved in fossilization, the most important being diminution of organic matter, diminution of phosphate, and increase of carbonate of calcium and increase of fluorine; and the latter is found to be decidedly the most reliable indication of antiquity. This principle is then tested by an extended series of analyses grouped in chronological order, and showing in each case, besides the organic matter and iron oxide, the proportions of P_2O_5 and F, the proportion of F which apatite having an equal amount of P_2O_5 would contain, and the ratio of the F in bones to that in an equivalent quantity of apatite. This ratio is made the real point of distinction, and, in spite of minor irregularities, it exhibits a good gradation as we pass backward in time from the Quaternary to the Silurian fossils. The averages for each formation are as follows: Modern, .058; Quaternary, .36; Pliocene, .58; Miocene, .61; Oligocene, .59; Eocene, .70; Cretaceous, .92; Jurassic, .91; Triassic, .89; Permian, 1.06; Devonian, .98; Silurian, .94. The averages for the geologic eras show a more perfect gradation and indicate the extent to which this criterion can be used with confidence: Modern, .058; Quaternary, .360; Tertiary, .620; Mesozoic, .907; Paleozoic, .993; normal apatite, 1.000. The cause of the increase of fluorine in fossil bones is found in the fixation of the fluorides dissolved in percolatng waters. The synthesis of apatite at high temperatures is well known; but Carnot's exper-

iments prove that the affinity of calcium phosphate for calcium fluoride leads to the formation of apatite in the wet way also, and the fixation of F continues until the proportion found in apatite is reached. To further substantiate this explanation analyses are cited to show that F is very generally present in natural waters. The paper closes with a practical application of Carnot's principle. A human bone was found with bones of the Mylodon and several other extinct animals at Natchez, Mississippi, under conditions which left room to doubt whether the man was really a contemporary of these animals. Analyses were therefore made according to Carnot's method, by R. L. Packard, of the human bone and bones of the Mylodon. The definitive ratio was found to be .12 for the Mylodon and .20 for the human bone. This proves them to be approximately coeval and to belong to a period between the present and Quaternary.

On Some Dikes Containing Huronite. By A. E. Barlow. *The Ottawa Naturalist*, **9**, 25–47. — This mineral, which occurs as porphyritic crystals in diabase dikes and bowlders at many points in the part of Ontario adjacent to Lakes Huron and Superior, has been variously described and classified by previous writers, but it is now found to originate in the alteration of a basic plagioclase (labradorite) and to be closely related to saussurite. One of the least altered of the labradorite phenocrysts, of sp. gr. 2.679, was analyzed by Dr. B. J. Harrington, of McGill University, with the following result: SiO_2, 54.19; Al_2O_3, 28.42; Fe_2O_3, 0.77; FeO, 0.41; MnO, trace; CaO, 10.47; MgO, 0.52; Na_2O, 4.47; K_2O, 0.63; loss on ignition, 0.59 = 100.47. A typical example of the Huronite gave N. N. Evans, of McGill University: SiO_2, 47.07; Al_2O_3, 32.49; Fe_2O_3, 0.97; CaO, 13.30; MgO, 0.22; K_2O, 2.88; Na_2O, 2.03; loss on ignition, 2.72 = 101.68.

On Lawsonite, a New Rock-forming Mineral from the Tiburon Peninsula, Marin County, California. By F. Leslie Ransome. *Bull. Dept. of Geol. Univ. of Cal.*, **1**, 301–312. — This new species is a light-colored orthorhombic hydrous subsilicate of aluminum and calcium, occurring abundantly in a crystalline schist and in veins of margarite traversing the schist. The crystallographic and optical properties are described at some length. Two analyses are then given; the molecular ratios are calculated from these, and the following theoretical composition is deduced from the formula thus obtained: SiO_2, 38.09; $Al_2O_3 + Fe_2O_3$, 32.69; CaO, 17.77; H_2O, 11.45 = 100.00. The water is undoubtedly constitutional, as the loss at a temperature of 225° C. was only a little over 0.1 per cent. The following is suggested as the probable structural formula:

$$(HO)_2 = Al - SiO_3 - Ca - SiO_3 - Al = (HO)_2.$$

On Analcite Diabase from San Luis Obispo County, California. By Harold W. Fairbanks. *Bull. Dept. of Geol. Univ. of Cal.*, **1**, 273–300. — This paper describes three quite widely separated occurrences, in dike form, of a rock related to theralite or teschenite, but provisionally called diabase, and characterized by a large percentage of secondary analcite. An analysis of one of the dikes by V. Lenher gave: SiO_2, 50.55; Al_2O_3, 20.48; Fe_2O_3, 2.66; FeO, 4.02; CaO, 7.30; MgO, 4.24; K_2O, 2.27; Na_2O, 8.37; H_2O, .44; Cl, trace = 100.33. Analyses of a typical teschenite, a theralite, and a plagioclastic elæolite syenite are quoted for comparison.

Notes on Minnesota Minerals. By Charles P. Berkey. *Twenty-third Annual Report of the Geol. and Nat. Hist. Survey of Minnesota*, for 1894, 194–202. — An analysis of the amygdaloidal diabase of Grand Marais afforded: SiO_2, 55.40; Al_2O_3, 22.55; Fe_2O_3, 14.67; FeO, 3.75; MgO, .74; CaO, 1.41; H_2O, .97 = 99.49. Three minerals found in this rock were also analyzed, as follows: Apophyllite — SiO_2, 52.61; Al_2O_3, .67; Fe_2O_3, trace; CaO, 25.22; MgO, .17; K_2O, 3.03; Na_2O, 1.71; HF, trace; H_2O, 16.17 = 99.58. The Al_2O_3 and Fe_2O_3 are probably due to minute needles of laumontite. Laumontite — SiO_2, 53.87; Al_2O_3, 18.06; Fe_2O_3, .88; CaO, 11.19; MgO, .45; K_2O, .29; Na_2O, .67; H_2O, 13.18 = 98.59. Strigovite, a green, chloritic mineral — SiO_2, 13.14; Al_2O_3, 13.22; Fe_2O_3, 24.20; FeO, 12.19; CaO, 1.50; MgO, 3.49; H_2O, 12.34 = 100.08. A compact, nodular form of datolite gave: SiO_2, 36.90; Al_2O_3 and Fe_2O_3, 1.51; CaO, 35.67; B_2O_3 by difference, 20.32; H_2O, 5.60 = 100.00. Two analyses of travertine are given — one derived from a limestone at Minneapolis, and the other derived from a typical dolomite near Osceola, Wisconsin:

From limestone — $CaCO_3$, 98.01; $MgCO_3$, 1.44 = 99.45.
From dolomite — $CaCO_3$, 98.20; $MgCO_3$, 1.75 = 99.95.

These facts are supposed to have a bearing upon the derivation of dolomite from limestone. — A shell marl from a slough at Fergus Falls gave: Insol., largely SiO_2, 4.010; $Al_2O_3 + Fe_2O_3$, 1.160; $CaCO_3$, 89.744; $MgCO_3$, 4.480; $Ca_3P_2O_8$, .275; loss and organic matter, .333 = 100. The same report also contains (203–214) analyses of the following substances: Pyroxene, from an augite-soda granite; native copper; iron ore, from the Mesabi Range; green felsite; anorthite, from a cave near Splitrock Point, L. S.; supposed bog manganese (really peat); mineral water, from a well 500 feet deep at St. James; augite-soda granite; anorthoclase, from the augite-soda granite; hornblende porphyrite; the Winnebago meteorite, taken as a whole; the iron of the meteorite; the rounded pellets of the meteorite; quartz porphyry; Saganaga granite; fine-grained gabbro, or "muscovado;" taconite (sideritic chert); silica-kaolin; glauconite.

Lead and Zinc Deposits of Missouri. By Arthur Winslow, assisted by James D. Robertson. *Reports Missouri Geol. Survey*, 1894, 6 and 7, 21 + 763. This voluminous and finely illustrated report is in reality a complete account of the history, compounds, modes of occurrence, distribution, and industry of lead and zinc throughout the world, the object of the authors having been to make this a general work of reference on lead and zinc, with Missouri as a center. The original chemical contributions are found in the second volume (VII), and chiefly in the chapter on the composition and origin of the Missouri deposits (pp. 441–487). Among the gangue materials or matrices of the ores analyses are given of the so-called tallow clays and the secondary cherts. The former are very characteristic, and may be regarded as, essentially, intimate mixtures of highly ferruginous kaolin and silicate of zinc. The proportion of zinc oxide is commonly from 20 to 40 per cent., the highest value given being 56.12 per cent. The secondary cherts, which represent a general silicification of the deposits subsequently to the formation of the ores, are composed principally of amorphous, chalcedonic silica, with small proportions of metallic oxides and residuary carbonates of calcium and magnesium. Passing to the ores, there are numerous complete analyses of sphalerites, calamines, smithsonites, galenites, and cerussites. It is inter-

esting to note that many of the sphalerites are cadmiferous, as might be inferred from the frequent coating of greenockite, and that the galenites run very low in silver, the highest determination being 4 ounces per ton. There are also analyses of the superbly crystallized calcites and the abundant barites. — In the discussion of the origin of the ore bodies Mr. Winslow accepts the view that the component minerals, including the ores, have been derived chiefly from the inclosing and overlying rocks, and not from a great depth in the earth. To place on a firm foundation the fundamental proposition that the country rocks are a possible source of the ores, several series of analyses of the Missouri rocks were made with great care by Mr. Robertson. It was thus proved that the Archæan rocks, including granites, porphyry, and diabase, contain in every instance appreciable proportions of lead, zinc, copper, and manganese, besides barium sulphate. The same is substantially true of the Silurian magnesian limestones and of the Carboniferous limestones, although in some cases the samples were taken at points far removed from any known ore deposits. The proportions of the various metals removed from pulverized samples of the rocks in a given time by different solvents were also determined. Averaging the metalliferous contents of the limestones, we obtain the following results:

0.001009 per cent. metallic lead = 0.00117 per cent. galena (PbS).
0.00239 per cent. metallic zinc = 0.00359 per cent. blende (ZnS).

This is equivalent to 0.00198 pound of galena to 1 cubic foot of rock, and 0.00603 pound of blende. From this the contents of different areas are as follows:

87.0 pounds of galena per acre 1 foot thick.
27.8 tons of galena per square mile 1 foot thick.
13,900.0 tons of galena per square mile 500 feet thick.
261.0 pounds of blende per acre 1 foot thick.
83.6 tons of blende per square mile 1 foot thick.
41,500.0 tons of blende per square mile 500 feet thick.

In other words, the metalliferous contents of 500 feet of limestones covering about 3 square miles is equal to the annual production of lead and zinc ores in Missouri, and it thus appears that the country rocks are an ample source of the metals in the ore deposits. — The report closes with an appendix, by Dr. E. O. Hovey, on the cherts of Missouri. The examinations were both chemical and petrographic, and the conclusion is drawn from the twenty-three analyses that the cherts consist essentially of chalcedonic silica, with only traces of opal or amorphous silica, the silica being, in general, quite insoluble in caustic potash.

Clay Industries of New York. By Heinrich Ries. *Bull. N. Y. State Museum*, 3, 97–262. — This is a comprehensive account of the clay deposits of the State and their products. In general, the detailed description of each deposit is accompanied by one or more chemical analyses, but these are not tabulated or compared, so as to develop any facts of special interest which they might exhibit.

Preliminary Report on the Geology of a Portion of Central Ontario Situated in the Counties of Victoria, Petersborough, and Hastings, together with the Results of an Examination of Certain Ore Deposits Occurring in the Region. By Frank D. Adams. *Geol. Survey of Canada, Annual Report for 1892–93*, 6, 1–15 J. — This report includes several analyses of iron ore, and some half dozen assays of pyrite and pyrrhotite for gold, silver, and nickel, with uniformly negative results.

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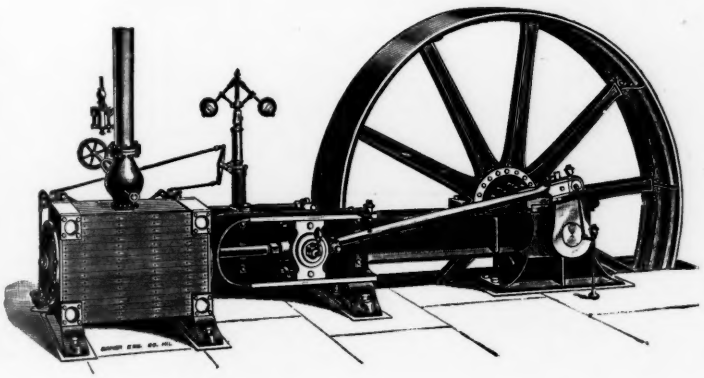

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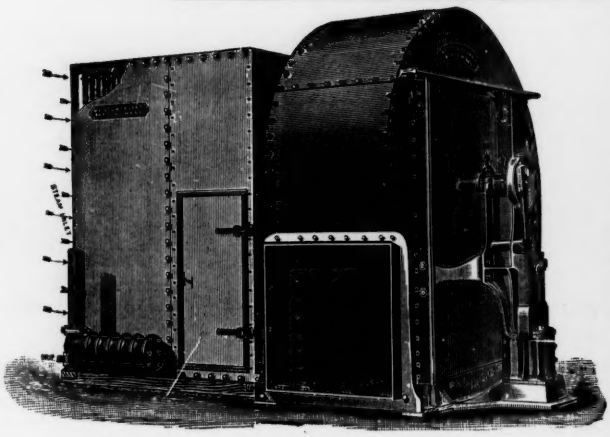

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